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A STUDY
OF
ELECTROTHERMAL AND ELECTROLYTIC INDUSTRIES

BY

EDGAR A. ASHCROFT

MEMBER INST. ELEC. ENGINEERS, LONDON; MEMBER INST. MINING & MET., LONDON; ASSOC. MEM. INST. CIVIL ENGINEERS, LONDON; MEMBER FARADAY SOCIETY, LONDON; MEMBER AM. ELECTROCHEM. SOCIETY; FORMERLY GENERAL MANAGER SULPHIDE CORPORATION (ASCHROFT PROCESS) LTD.; LATE MANAGING DIRECTOR PHOENIX PROCESS TRUST, LTD.

STATISTICS

By I. J. MOLTKEHANSEN

(DIPL. ING., BERLIN)

IN THREE PARTS



PART I

INTRODUCTORY

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PREFACE

THIS book is intended for the use of all classes of technical or commercial men, and students engaged in the young but rapidly growing industries of electrochemistry and electrometallurgy.

Although such a book can be little more than a rearrangement of matter already published in various forms, I hope nevertheless that it will fill a want not yet adequately filled by existing text-books, of which none is an entirely practical and comprehensive handbook.

The great lack of really practical information about nearly all industrially successful processes in electrometallurgy and electrochemistry, outside of that possessed by those practicing the various specialized branches of the industry, is due to our commercial conditions, which make it necessary for individual producers to jealously guard their secrets from their competitors, to the great detriment of the advance of the industries as a whole. In such a situation there are necessarily very few people possessing an extensive practical knowledge on a particular subject who are likely to write about it.

The author hopes that a somewhat unusually wide and varied experience in more than one branch of these industries places him in a favorable position in this respect and will consequently lend to the book a wider utility.

The general arrangement of the book has been the subject of much thought, and is on a somewhat novel plan.

The general division is into three parts, of which the present volume (Part I) deals with all the more general aspects of the subject. A fair acquaintance with the principles of chemistry, physics, engineering and some elementary mathematics is of course assumed, but unnecessary mathematics has been avoided, while only a brief summary of all important leading principles of theory has been attempted, for the benefit of those whose knowledge of elementary science has become rusty.

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The arrangement of Parts II and III, containing all the industrial operations of electrometallurgy and electrochemistry, is alphabetical, with respect to the several elements whose liberation from their compounds is, usually, the aim of the industrial process under consideration. When the product sought is not an element, it is either an alloy of metals, a special chemical compound, or a simple admixture. This class of products is so small numerically that it seemed advisable to classify them in the alphabetical series with their most prominent constituent element; thus carbides are placed under "Carbon," chlorates under "Oxygen," brasses under "Copper," etc.

The subdivision of the elementary classes is important. First a fairly comprehensive account of the element will be given from the standpoint of its chemical and physical properties, including tables of all its important compounds and their various data. In compiling such data it has been my object to include all those likely to be of actual use to practical workers or experimenters, and so to constitute this part of the book a work for ready reference. Next I shall give an account of the natural sources of the element and the actual processes employed for winning it to-day. Thirdly, a somewhat shorter account of older and of unsuccessful competing methods, patents, etc., which I shall class all together under the heading "Other Methods, Suggested, Superseded, or Historical."

In a continually evolving industry whose every economic landmark is apt to shift from year to year with kaleidoscopic frequency and bewildering disregard of consequences, some such classification seems peculiarly desirable, because the barely suggested process of yesterday has often been, and may again be, the regularly worked process of to-morrow, and even exploded ideas are often resuscitated when changes in controlling conditions alter the unstable balance of economic results.

Let no one feel aggrieved, therefore, if his work is placed under this heading. The sole consideration, which will guide me in assigning such a place to any process, patent or idea will be the actual fact of whether the process is known to be worked or not *to-day*. Such a classification, although it will, like poverty, sometimes bring strange bedfellows together, is essentially better in my opinion than if I were to essay the difficult task of discrimination, as some authors have done, constituting

myself judge, jury, professor, practical worker and prophet all in one.

Finally, where a sufficient interest attaches to the metal or product a very brief historical sketch of the industry will be added.

The above classification will be rigidly adhered to throughout Parts II and III, and I venture to hope that it will prove more serviceable than older methods of classification under such headings as Fused Electrolysis, Solution Processes, Furnace Methods, etc., which are confusing and appear to me to be inadequately distinguished between themselves.

Alternate-current electrolysis is so novel a subject that it can be dealt with in a single chapter, and the same remark applies to organic electrolysis.

I am greatly indebted to many distinguished friends as well as to the standard literature on these subjects for assistance in compiling this work, and I am glad to acknowledge the same under the respective headings.

Mr. Ivar J. Moltkehansen has collaborated with me in the preparation of statistics for the volumes.

THE AUTHOR.

BALESTRAND, NORWAY, *February*, 1909.

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CHAPTER I.

HISTORY.

AN APPRECIATION.

HIDING behind an impenetrable veil of mystery, the forces of nature have worked their relentless destinies unremittingly and unchanged, since the unknown and unthinkable origins of their being.

Whatever the precise order of events in the grand cosmological drama of creation; whatever the true interpretation of the periods of the geological epochs; whatever the real order and nature of the origins of organic species; whatever the origin and destiny of the human intelligence; one thing is now fixed, and endowed with the quality of certainty in its relation to the human understanding. This fundamental truth is the undisputed and absolute reign of objective law and order in the universe in which we live.

However imperfectly we may apprehend the laws of nature (and our understanding of them is frequently subject to modification, and as far as we can possibly conceive, must always be imperfect); however limited may be our own powers and possibilities, we nevertheless perceive around us, in the light of this essentially modern conception, a world of order and decorum; a place in which the mind can calmly rest, whatever may be its own destiny, and not a realm of capricious uncertainty,—a madman's sea of dreams and contortions,—in which no anchorage can be found for the sane understanding.

The conception of the above fundamental truth, in all its full force and significance, marks a great gulf bridged between our

own time and all former times of the world's history. It is a new starting point for the human spirit. It opens, as it were, a new door to the aspirations and the hopes of man; and around the portals of this new opening are to-day crowding eager throngs of curious investigators, ever becoming more eager as fresh vistas of untrodden paths open out before them. We see these eager workers in many lands pressing forward into the unknown, impatient of any delay, on the *qui vive* for results. But in America particularly, charged as it is with young blood, — and perhaps too because it is less weighted than its contemporary nations with the débris of past ages and past mistakes, — this spirit of energetic curiosity has risen to a veritable frenzy of active research. At every university in the United States, in every cultured household, at every center of intellectual activity, this spirit is dominant. It is even becoming a serious question whether such frenzied activity, such "strenuous life" of the mind, is permissible in the healthy and rightful regulation of human conduct, with a view to the permanent welfare of the race.

Be this as it may, a veritable passion, alike of discovery and of its twin brother, industrial development, has been aroused; and, wise or foolish, will doubtless, like other human passions, burn itself out to fruition or to exhaustion; mayhap to both.

If we reflect on the curious history of the human race, even in the most casual manner, we cannot but be struck with two very remarkable facts. The first is the great antiquity of civilizations; societies and organizations, in most respects akin to, and apparently all but equal to our own, are not a thing of yesterday. Such civilizations have arisen more than once before in the world's history and then passed away, replaced by an order of life more barbarous or more primitive; such for instance was the marked retrogression of knowledge and its attendant civilization during the period known as the Middle Ages, only a very few centuries back in the vista of time. The second noticeable fact is the extremely short space of time during which exact knowledge of a truly scientific order, based upon observation, experiment, and objective reasoning processes, has replaced the erratic guess-work of genius, the dreams of poets, and the enthusiasms of individual actors on the stage of life, as the guiding principle of human actions.

Full three thousand years before Buddha or Confucius walked this earth, and six hundred years longer still before the brief and dramatic scenes which marked the dawn of Christianity, Egyptian and Babylonian civilizations flourished, in which human life in all its essential comforts and conveniences, and in much of its intellectual activity, at least for the few, was as perfect as, or more perfect than it is in Chicago, New York, Paris, Berlin, or London of to-day. There is no essential novelty in the intellectual activity of this age that has not found a parallel at least once in the world's history before. Even whilst Christ was preaching the doctrines destined both to move the emotions of men, as no teaching has probably moved them before or since (and also, through inherent limitations and misapprehensions, destined to eclipse the light of scientific discovery for many centuries), the light of true knowledge was kindled, and had been burning for several centuries in the heart of a pagan civilization in Alexandria. Doctrines as to the nature of the universe, closely approximating our very latest scientific acquisitions,— doctrines for the holding of which mediæval men were persecuted and put to death by the very Christian authorities whose professed mission was to enlighten the world, — had been clearly understood in Alexandria several hundreds of years before. The light of science here (and also probably in the older and forgotten times of earlier Chinese and Eastern civilizations) flamed for a time and then went out to a mere flicker in the socket, and remained so eclipsed for long, long centuries.

This lamentable result, occurring more than once in history, has been apparently due to the lack of proper correlation and objective order in the researches of men in former times. Life was always based on some personal foundations. Theocratic, royal, aristocratic, military, or individual theories and ambitions, in all the multitudinous varieties which history reveals to us, were all that could be found to fill the place of nature's real demand; namely, an absolutely impersonal (universalist, or realistic) spirit to govern those who will pry far into her secrets, or tear aside the veil from her mysteries and build a lasting temple of knowledge. This spirit has been in a measure found in modern times; and to this circumstance, in one form or another — a circumstance which it seems to me is but little understood in all its mighty import as yet, even by the priests

of this new religion, the men of science — we may trace all the permanent progress which marks our era, and will cause it to stand prominently out on the page of history as no former age will stand. Though but a few centuries have elapsed since Gallileo was persecuted and Giordano Bruno was being burned at the stake for holding the doctrines of the Copernican astronomy; though barely three centuries have passed since the very discovery of electricity as a forçe of nature, and barely a century since the foundations of our science of electro-chemistry were laid by the great work of Sir Humphry Davy at the Royal Institution in London, yet during that short time, so vast a body of correllated fact and definite experience has been accumulated that it is quite unthinkable that the wave of enlightenment should ever again recede into the night of ignorance.

From this remarkable rapidity of development it arises that the record, in any truly historical sense, of scientific discovery, and more particularly of its very latest chapter, "electricity," cannot yet be written. No sufficient distance can be gained from the events to get a true perspective. The whole matter is practically one of present-day experience. All but unnoticed by the untechnical observer, are happening all around us to-day, the events which, leading to great developments in every industry, will form the main body of the history of an important aspect of this world's future.

A few facts, however, may be noted as to the origin of our special subject which will serve as landmarks of some value.

No mention of electrolytic phenomena has come down to us from the Alexandrian period of scientific enlightenment, nor from any other early age,[1] and the very first we hear of such observations is the study of the striking effects of frictional electricity, which began to attract some attention about the middle of the eighteenth century. Some very large machines were constructed, one of which is still in the Museum at Haarlem. About one hundred and thirty years ago Pater Beccaria succeeded in reducing the oxides (revivifying the calxes, he called it) of certain metals in minute quantities by the use of such

[1] If we except a few isolated observations, such, for instance, as the coating of iron with copper by immersion in copper sulphate solution, which, according to Titus Ulke (Modern Copper Refining) was observed by one Zosimus about the seventh century A.D.

machines. This is probably the first recorded electro-chemical experiment; the metals experimented with successfully were zinc and mercury. Later on, Priestly, and then Van Murum conducted experiments with the electric spark by passing it through gases. In this way the formation of ozone was first discovered. The first actual electrolysis of water is said to have been made by Diemann and Paets Van Troostwyk, also in Haarlem, in 1779.[1] Sparks were passed between two wires sealed into a glass tube, and the gases, oxygen and hydrogen, duly appeared at these electrodes, but of course the gases were mixed. Ritter modified this experiment and conducted what was probably the first electrolysis of a silver salt, obtaining metal deposits on the cathode.

Closely after this pioneer work follows the famous discovery of Volta's pile. This was in 1800, and from that date the true science of electro-chemistry has its birth. Volta actually decomposed water and collected the separated gases. Many workers with Volta's apparatus began to accumulate experimental data, Nicholson and Carlisle decomposed salt solutions and remarked the formation of acids and alkalies at the electrodes.

Then followed the brilliant work of the young chemist, Sir Humphry Davy, who, with the large battery of one hundred and forty-four cells of carbon in nitric acid and zinc in sulphuric acid, constructed for his use by the Royal Institution, successfully decomposed, first potassium, then sodium, magnesium, barium, and other oxides and hydrates. It is recorded how intense was this experimenter's delight when first the globule of potassium appeared at his platinum wire electrode, revealing an entirely new metal and confirming his previous, dimly perceived theories. Such moments can be better appreciated than described by all who have felt the fascination of experimental research.

Davy's pupil and successor, Michael Faraday, who followed up his master's work assiduously, formulated his great law, explanatory of the chemical effect of an electric current. As every tyro now knows, this law asserts a definite quantitative relation to exist between the value of current passing in any electrolyte and the chemical effect produced. This law, which

[1] Arrhenius, Text Book of Electro-Chemistry.

is of the nature of an elementary and fundamental conception illuminating the whole area of the subject, has greatly helped in the formation of a rational and intelligent science of electro-chemistry.

As far back as 1811, Wollaston, who did some work on the improvement of Volta's idea, had exhibited before the Royal Society the glowing of a platinum wire, when traversed by an electric current; and many other experiments are recorded by various workers; but many years elapsed before these isolated phenomena were explained, or connected by any intelligible laws of sequence. It was in 1840 that Joule, of Manchester, first formulated the great law which bears his name, and relates to the heating effect (called also the Joule effect) of an electric current.

This law asserts the existence of a definite mathematical relation between the quantity of electricity passing in a conductor, and the thermal effect thereof. Like Faraday's law, it is of an elementary and fundamental nature and importance.

By these two laws (Faraday's and Joule's) nearly all of the modern practice of electro-chemistry and electro-metallurgy is governed. It was in 1834 that Faraday communicated his most famous conclusions relating to electrolytic theory, and christened the electrodes and the constituents of the electrolyte, cathode and anode, and cations and anions respectively. The way for this brilliant physicist's illuminating discoveries had been prepared by the work of the illustrious scholar and mathematician, André Marie Ampère, who lived between 1775 and 1836, publishing several important contributions to the theory of electro-dynamics; and also by the earlier researches of Charles Augustin de Coulomb (1736–1806), famous for his work in connection with the dynamics of magnetic and electric attractions.

Those two giants of scientific discovery, and especially of mathematical reasoning, Helmholtz and Clerk-Maxwell, also Clausius, Kohlrausch, and many others of lesser note, brought the science by numerous irregularly proportioned steps into its more modern position, a position which ranks high in importance and interest amongst the sciences which afford to mankind theoretical explanations of nature's secrets.

A numerous army of practical experimenters and men of inventive genius soon began to turn these principles to practical

account. The first great practical application was found in the industrial plating of gold and silver on baser metals, and this was rapidly followed by the practical development of Jacobi's original (1839) invention of electrotyping and of the kindred arts, then by the plating of nickel and other metals. Then the art of electrolytic copper refining, which was originally due to Elkington, and dates from 1865, rapidly assumed large proportions with the advent of the dynamo-electric machine in 1867.

From that time forward the development of the copper refining industry has been steady and continuous; its success in the present day is such as to practically exclude all other methods for the final purification of copper and recovery of the precious metals alloyed therewith, from consideration. The next large development began about twenty years ago, when the foundations of the electrolytic aluminium industry were laid by Bradley, Cowles, Heroult, Hall, and others, and of the electrolytic alkali and alkali metal industry by Hamilton Young Castner, Solvay, Hargreaves and others. The year 1891 also brought the discovery of artificial abrasives, and a few years later the Niagara carborundum factory started operations, and some European factories were organized for these industries (many of the latter have, however, since disappeared). Artificial graphite was produced by the Acheson process some years previous to 1889, and a company organized early in that year commenced the industrial production which has continued ever since at Niagara Falls. In 1892–3 also the first industrial production of calcium carbide was brought about at the Wilson aluminium works at Spray, N. C., and between that date and the present this industry has grown to large dimensions both in America and in Europe. During the same time was more slowly developed the industry of potassium and sodium chlorate manufacture, which had been suggested at a much earlier date, and the industry of electrically produced phosphorous which was due to Messrs. Parker and Readman, H. A. Irvine and others.

Some account of the details of the historical development of each of these industries will be given under the headings of the Elements and Their Respective Products, in the second and third parts of this work.

The outlook at the present date for the extension of electrochemical industries is distinctly encouraging. For, even with-

out the hoped for materialization of such expectations as are held out to our more sanguine imaginations by the recent work in iron and steel production, nitrogen fixation, and sulphide ore treatment, they are evidently destined to fill a very prominent place in the activities of the next few decades. With the successful advent of the three industries I have named, and a more general application of the abundant cheap water powers available in certain countries, such as Norway (of which more will be said hereafter), a prodigious and unparalleled expansion may be looked for, practically heralding a new epoch in the industrial history of the world, — a change comparable only to some of the great epoch-making changes of history, when mankind has passed out of one, inferior, habit of life and into another and superior one.

All honor then to the members of this noble army of peace. I believe the day is not far distant when the name of science and discovery shall be honored amongst men as no name has ever yet been honored; that the pursuit of exact knowledge, and its applications, will ultimately lead to the satisfaction of the aspirations of mankind. Amidst the debacle of the older superstitious dogmas, and the failure of many cherished ideals, which it is the lot of mankind to experience to-day, the pursuit of practical science forms an intelligent, necessary, lofty ideal to which to direct the perceptions, attach the emotions, and with which to occupy, disinterestedly and usefully, all the energies of the human mind and body.

CHAPTER II.

THEORY OF ELECTROCHEMISTRY.

I.

WHEN a current of electricity passes anywhere phenomena occur, varying in kind according to the nature of the medium through which the electricity is passing. Three kinds of media are distinguished: (1) simple conductors, or resistors; (2) electrolytes; and (3) gases, or space. When passing through a medium of the first kind the electric current is always accompanied by an evolution of heat which takes place in direct proportion to the energy involved in overcoming ohmic resistance (Joule's law).

The resistance which a current encounters in a simple conductor is measured in ohms per cubic unit of substance. Ohm's law, which applies universally to all conductors, whether solids, electrolytes or gases, furnishes us with a mathematical relation between the electrical pressure, the electrical flow, and the electrical resistance; the latter being a specific natural quality which varies for different materials, and for the same materials at different temperatures, pressures, or other physical conditions.

Ohm's law may be stated thus: —

$$(A) \qquad \text{Electrical Flow} = \frac{\text{Electrical Pressure}}{\text{Electrical Resistance}}$$

$$(B) \quad \text{Electrical Resistance} = \frac{\text{Electrical Pressure}}{\text{Electrical Flow}}$$

$$(C) \quad \text{Electrical Pressure} = \text{Electrical Resistance} \times \text{Electrical Flow.}$$

Tables of the specific resistances of substances may be found in many standard works on electricity, and likewise some account of the origins of the various units of which I am about to speak. The modern unit of electrical resistance is the ohm. It corre-

sponds to the resistance offered by a column of mercury 106.3 cm. long and one square millimeter in sectional area at 0° C.

All electrical phenomena are due to the existence of electrical pressures known as potential differences between various points, which differences are, in their turn, due to the presence, or absence, of electrical charges. Hence originates the somewhat inaccurate, but expressive term, electromotive force, which is used to designate the immediate consequence arising from any potential difference. The unit of electromotive force is the volt. Like the ohm it is an arbitrarily chosen standard, its magnitude having a convenient relation (in the complete system of units) to the magnitudes representing electrical resistance, electrical flow, etc. The standard commonly employed in practical uses for absolute measurement of this unit, is a voltaic couple of special design, arranged for the purpose of securing accuracy and stability (standard cell). The element commonly used is the Clark cell; it has an electromotive force of 1.433 volts.

The coulomb (a derived unit) is the volume of electricity which is forced through a resistance of an ohm, by a volt of electromotive force, in a second of time. This unit when expressed as a "rate" (1 coulomb per second) becomes the more generally used standard of current, the ampere.

The watt (also a derived unit) or the electrical unit of power (power may be regarded as the "rate of doing work") is the direct product of the volt and the ampere.

At this point we encounter the mechanical form of energy; the most common of all its forms. Mechanical energy is measured in centimeter-grams, foot-pounds, ton-miles, or any convenient magnitude, representing a given weight lifted to a given distance, against the attraction of gravitation at the earth's surface. An energy "rate" is referred to the second, minute, hour, etc. The unit of mechanical force most commonly employed by scientific men is the dyne. It is the force which, acting on one gram for one second, would produce in the mass a velocity of one centimeter per second. It is also the force of attraction which the earth exercises on $\frac{1}{981}$ gram at its surface. When a given force has acted through a given distance, the spent energy is called "work." The scientific unit of work is the dyne-centimeter. The capacity for performing a given quantity of work in a given time is called "power." The unit of power com-

monly employed by engineers represents 33,000 foot-pounds per minute (1 foot-pound = 0.13825 kilogram-meter) and is called a horse-power. The common unit in electrical engineering is the kilowatt or 1000 watts. The centimeter-gram-second system of measuring energy in all its forms is now the basis of all scientific calculations.[1]

But energy, whether mechanical or electrical, may be expressed in terms of heat, and, so expressed, may be described as the quantity of heat required to produce a given temperature change in a substance of given weight and known specific heat.

The specific heat (a natural quality like electrical resistance, specific gravity, etc.) of nearly all substances has been experimentally determined, and tables are to be found in many standard works on heat, mechanics, etc.; water, the substance having the greatest known specific heat (or best heat storage capacity), is referred to as unity; all other specific heats are therefore fractions of unity. This quality represents in reality the relative quantity of heat which disappears, or reappears, in bringing about any given change of temperature in matter.

A natural quality of allied character is the latent heat of substances, or the heat which disappears, or reappears at a critical moment, occurring during any change of state, e.g., solid to liquid, liquid to gaseous, or vice versa. Data of latent heats of nearly all substances have also been experimentally determined and tabulated.

In comparing heat phenomena, it is often necessary to use an imaginary "absolute zero" which is 273° below the arbitrary zero of the centigrade scale. The necessity for this will become clear when considering gaseous phenomena, and the following important laws which govern them. It is the point at which all heat phenomena cease; presumably, therefore, it represents the point at which there is no heat, or at which the form of motion called heat is entirely stilled.

The units of heat energy which are used by engineers and chemists, the Calorie (large) and the calorie (small) are, respectively, the quantity of heat required to raise 1,000 grams of water, or 1 gram of water 1° C. (from 15° to 16°). The former measure, mostly used in France and other continental countries, is also called the kilogram calorie; the latter, mostly used in England

[1] For particulars of the various c.g.s. units see footnote to Chap. iii., p. 32.

and America, is called the gram-calorie. Still another unit, much used in Germany (particularly by Ostwald), and based on a standard of 100 gram calories is designated a kalorie (k). For scientific purposes it is a more logical standard because, by including a longer range of temperature change (0° to 100° C.), it more nearly, though still not perfectly, expresses the average behavior of substances, the specific heat of all substances being found to vary with the temperatures.

Finally, the joule is the unit of heat energy expressed in terms of electrical energy, or vice versa. It is therefore the unit in which two important forms of energy meet on common ground, and is respectively of a magnitude equivalent to one volt-coulomb (or one watt-second) of electrical energy, or .2391 gram-calories of heat energy. Conversely the gram-calorie is equal to 4.183 joules.

The units of electrical capacity (the farad), magnetizing force (the H. or dyne; per square centimeter unit) and others in common use in electrical engineering, do not play any prominent part in electrochemistry at present and are therefore not introduced here.

Three extremely important laws govern the behavior of all true gases in the physical world; and being the basis of many metallurgical calculations, must be referred to briefly here.

They are as follows: 1. Boyle's law, which asserts that the pressure of all true gases at constant temperatures varies directly as the volume; and vice versa. 2. Guy Lussac's law, which asserts that the volume of all true gases at constant pressure varies directly as the absolute temperature, and vice versa (it will be remembered that the absolute zero is 273° below the centigrade zero, so that the absolute temperature is ascertained by adding + 273° to the observed temperature). 3. Avogadro's law, which discloses the remarkable coincidence that each molecule of every gaseous substance has the same volume at constant pressures and temperatures.

The standard temperature and pressure employed in scientific calculations with gases is 0° C. and 760 mm. of mercury (= 29.93 inches bar.), and corrections are readily applied for all other volumes or temperatures. It is usual in writing chemical formulæ to express the number of molecules in a gaseous product by Roman numerals placed above the formula. If (as

throughout this book) the chemical formulæ and weights are interpreted as gram equivalents, every molecule of any true gas at standard temperature and pressure will occupy a volume of .02222 cubic meter. For a cubic meter of hydrogen, weighing 90 grams, and having a molecular weight of 2, it follows that a molecule of this gas occupies $\frac{2}{90} = .02222$ cubic meters. The same holds good for all other gases.

Thus action of steam upon metallic sodium.

$$\underset{36}{\overset{II}{2H_2O}} + \underset{46}{2Na} = \underset{80}{2NaOH} + \underset{2}{\overset{I}{H_2}}$$

The remarkably simple ratio of weights and volumes is here evident; 36 grams of steam occupying .0444 cubic meter, act on 46 grams of sodium (solid), and produce 80 grams of caustic soda (assumed solid) and 2 grams of hydrogen occupying 0.222 cubic meter, the atmospheric temperature and pressure being standard.

Joules law, which is fundamentally important in regard to the heating effect of an electric current, may be expressed thus:

Heat (in joules) = current (in amperes) $\times$ resistance (in ohms) $\times$ time (in seconds).

Calculations based on this and other laws will be discussed in the next chapter.

There are several other effects of the electric current connected with solid conductors besides the Joule effect. There is a difference of potential produced, and a loss, or gain (conversion), of heat energy at every contact of dissimilar metals; or of similar metals at dissimilar temperatures; or of metals and solutions; or of dissimilar solutions; or of solutions at dissimilar temperatures. There are special effects due to polarization, which may at times complicate observations. There is also the large range of magnetic induction effects; the obscure alterations which occur in the structure of metals when used for long periods as conductors, and many other noteworthy and interesting phenomena. But these all lie outside our present subject, either by reason of the smallness of the effects, which relegates them to the regions of purely scientific interest, or, as in the case of the magnetic and thermo-electric effects, they form an entirely distinct branch

of electrical engineering with which we are not at present concerned.

When electricity passes through the second and third class of media, referred to above (electrolytes or gases), the Joule effect is also always present, and Ohm's law is as truly applicable to the body of an electrolyte, or the actual path of the discharge in gases, as it is to solid conductors. But in these cases other important effects also occur and must be now considered.

II.

When electricity is passing through an electrolytic medium, disruption of chemical affinities is the result. This result occurs in consequence of a contact effect, which takes place at the surface of the electrodes, where they touch the conducting electrolyte.[1] This effect, formerly known as the Volta effect, as far as it concerns our subject to define it here may be described thus. It is a step up or down in electric potential, which occurs at every contact of an electrode with an electrolyte. In practice the effect is always observed in a double relation (pairs of phenomena); for, unless such a pair occurs, the inherent natural conditions are such that, no circuit being established, no current can exist. Any change of potential resulting under such conditions could only be observed with very special instruments and under carefully guarded conditions. It is manifest that every electrolyte which forms part of any electric circuit must have such dual conditions, for the current which enters, must also leave the electrolyte. This is equally true in cases of local action, (short circuits or any of the numerous electrolytic effects with which we are familiar); but in such cases, owing to the inherent conditions governing all electro-

[1] This effect must not, however, be confused with the so-called phenomena of "transfer resistance." The latter, quite a small effect, is a special form of resistance or impedance occurring at the actual point of juncture between an electrode and a solution. It is in fact the thermo-electric effect causing an absorption of heat energy at certain junctions and liberation at others. Conflicting experimental results have been obtained on this point. For the practical purposes of the present subject it may safely be neglected, for not only are the magnitudes exceedingly small, but also, in the case of the ordinary conditions of an electrolytic cell, the anode effect will always be in opposite sense to the cathode effect, and so neutralization will occur.

lytes, every pair of points neutralizes itself, and the separate potential effects are thus not very readily visible. When any part of any circuit is taken outside the bath of electrolyte, a pair of electrodes, and all the double phenomena of electrolysis result immediately. The net effect of the sum of every such pair of potential steps on a circuit is to either promote, or retard, the flow of current therein, to an extent dependent on the nature of the chemical substances which are brought into contact at the electrodes; that is to say, on the relative magnitudes and signs of the electromotive forces which appear at the two points of contact.

Actual chemical decomposition, or recomposition, of the constituents of the electrolyte and the electrodes occurs. When the outer circuit is broken, the decomposition which momentarily occurs on establishing these conditions is minute in quantity, and almost as soon as the effect occurs, all further rearrangement of atoms and molecules (or ions) ceases. When, however, a current exists in the outer circuit, the momentary effect is continually renewed by the removal of the electric charges (which otherwise accumulate at the electrodes), and normal conditions of electrolysis result. It will be manifest that these conditions are unaltered whether the current in the circuit is promoted from within the bath, as in the case of the galvanic cell, or from without the bath, as in the case of the electrolytic cell. In the former case the charges of electricity delivered at each electrode from the constituents of the dissociated or recombined ions are the "fons et origo" of the current, and the effect and measure of the energy thereof appear as potential difference at the poles. In the case of the electrolytic cell, a similar potential difference contributes to, or detracts from, the influences which promote the current from the outside circuit, and chemical changes (likewise corresponding to the current, and the sum, or difference, of these potential differences) take place.

The ultimate causes of the observed electrolytic effects are still obscure (as in fact are the ultimate causes of most physical or chemical effects), but we know that this one also takes place in accordance with constant laws. The amount of each elementary substance, or compound-radical, so liberated is in this case directly dependent on the quantity (or volume) of electricity involved.

Faraday's law, elaborated later by Maxwell, and of funda-

mental importance to the subject of electro-chemistry, declares that the quantity of any element, or compound-radical (ion) set free by a current of electricity, is "solely dependent on the quantity of electricity, and is independent of the voltage, the size of the electrodes, their distance apart, the concentration, or temperature of the electrolyte, and the strength of the affinities of the specific compound of the element being decomposed."

This law, though frequently questioned, has never been disproved, and rests to-day on a more solid basis than ever. We may, therefore, regard it as fundamental for all purposes of electro-chemical calculation.

In every passage of electricity through an electrolytic medium, however, there is also a simultaneous production of heat in the electrolyte, and also in the electrodes, which takes place (just as in the solid conductor) in direct proportion to the product of the energy involved in the passage of the current through each part of the circuit, and the ohmic resistance. In other words, the energy used in producing heat in any part of any electric circuit is proportional to the current squared multiplied by the resistance of that part and the time (Joule's law). Therefore, after allowing for a definite amount of energy, corresponding to the sum of the chemical energies of combination of the particular substances, separated or united at the electrodes in any electrolyte, a varying amount of surplus energy is always expended in producing heat in the electrolyte, and the magnitude of this effect will depend upon several factors, such as the size and specific resistance of the electrolyte and the electrodes, the rate of deposition, etc.

In the simple case first referred to above (the passage of electricity in a solid conductor), there is a direct mathematical relation which enables us to simply multiply the units of quantity (coulombs) passing during a given time and expressed then as a rate (amperes), by the units of electromotive force (volts), or the parallel mathematical equivalent, which is the amperes squared, multiplied by the units of resistance (ohms), whereby we obtain a like result in units of electrical heat (joules); and thus to obtain the result in units of electrical power (watts). Now the watt may be equally well expressed in units of mechanical power, for 1 watt is equal to .00134 h.p. and conversely 1 h.p. (or 33,000 lbs. raised1 ft. in 1 minute) is equal to 746 watts.

Or, again, it may be equally well regarded as a "potential rate of evolving heat" and be measured in heat units, for 1 joule is both the equivalent of 1 watt-second, and of .24 gram calorie. A kilowatt-year is therefore equivalent to 7,568,640,000 calories of heat production, or of 1,395,023,675,000 foot-pounds of mechanical energy production.

When a current is forced through an electrolyte, at least two kinds of energy absorption occur. First the ohmic effect, which is similar to that in the solid conductor, and then the electrolytic effect, which is dependent on the thermal energy of the chemical constituents of the electrolyte and of the electrodes. By the aid of Faraday's law, and knowing the thermal energy of any compound, we may now readily determine, first the electrochemical constants, or equivalent weights, liberated by a unit of current, and then the other element, viz., the electrical energy concerned in the reaction which is called the critical (or theoretical) voltage of dissociation. These and other calculations will be discussed in the next chapter.

The thermal effects of the current appear therefore comparatively simple and direct, whilst the electrolytic effects seem much more complex. The simplicity in the former case is however more apparent than real, for we really know nothing at all of the actual internal mechanism of the passage of electricity in conductors, and its conversion into heat energy. The very apparent simplicity of this phenomenon, like the apparent simplicity of the universal phenomenon of gravitation, seems to place it beyond further investigation at present.

Such conceptions as we have been discussing, moreover, do not explain the nature of electricity, heat, or mechanical energy; but they represent the inner boundary of our sphere of knowledge. Now, one of the greatest generalizations of the age, the great law which postulates the correlation of all the physical forces, helps us to apply the mechanical principles of mathematics to our experimental observations on the physical and chemical relations of nature. For although we are, apparently, as far from knowing what heat, electricity, chemical action, or gravitation really are, as was any mediæval engineer — fitting his pet machine with a diamond surreptitiously bathed in moonbeams, for its principle axle, in obedience to some alchemistic superstition — yet we now know quite cer-

tainly that a given quantity of electricity, flowing through a given resistance, is *always* produced by a given potential difference, and in its turn *always* produces a given quantity of heat, or of chemical action. We know that every material body or substance has a certain quality called its specific heat, and that this quality represents the power of storing, as it were, a definite quantity of heat, for every gram of the substance, and for every degree of rise of temperature. If heat is pumped in, the temperature of that body rises; if it is abstracted, the temperature falls; and we know that the rise or fall is directly proportional to the specific heat of that body. We know many similar things relating to the latent heat of liquids and gases, the contact heat, and contact potential, of solids; and the direct conversion of thermal into electrical effects, which occurs at the heated junctions of dissimilar metals. We know, in the relations of mechanics, that a given mass of a given substance *always* exerts a given pull on any other given mass or substance. We know that one molecule of any true gas occupies *always* the same volume at equal temperatures and pressures, and that gaseous volumes are proportional to their absolute temperatures and their pressures, and vice versa. And finally we know that an important correlation of all these phenomena can be expressed, by the aid of the principles of thermodynamics, in mathematical terminology, and will then be inevitably governed by mathematical laws.

There is a striking analogy between the behavior and properties of the various forms of energy we are here considering. Thus all heat phenomena may be regarded as primarily due to the existence of differences of "heat potential," or temperature between various points, and the tendency which these differences of temperature, like differences of electric potential, have to promote the flow of heat into or out of bodies through heat resistance. The specific heat of any body also offers a close analogy to the phenomenon of electric "capacity." Again, all mechanical energy may be referred to the action of gravitation, and the flow of energy resulting from various weights or pressures, acting through resistances (represented by distance and mechanical friction), and conditioned by resilience, elasticity, hardness, etc. But this line of thought would quickly lead us very far beyond our subject.

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III.

In studying electrolytic phenomena the nature and composition of the electrodes is of primary importance. In general, two classes of electrodes may be usefully distinguished, the soluble and the insoluble. This distinction applies mainly to the anode,[1] the cathode[2] being nearly always insoluble, and usually deposited upon. It is usual to state that the solution of an electrode takes place at the positive (or anode)[1] termination of the exterior circuit, whilst at the other terminal (or cathode)[1] the reverse process, that is a deposition, occurs; but although, in the majority of cases, this is actually what occurs, it is, nevertheless, scarcely a correct or allowable general statement in the present position of our knowledge of the whole subject. The only reason the anode dissolves, and not the cathode, is not directly connected with the phenomenon of electrolysis, but is solely due to accidental circumstances, and simple experiments can easily be devised to reverse the otherwise rather prevalent condition of anode solution and cathode deposition. For instance, if we electrolyze a solution of common salt with a platinum or a graphite anode, and a cathode of any conducting substance which is readily soluble in weak caustic soda solution, the cathode, and not the anode, will be attacked. In similar manner, when dilute nitric acid is electrolyzed with lead electrodes, and some lead in solution as nitrate, lead peroxide is deposited on the anode, and the cathode is free to dissolve in the weak nitric acid.[2] Amongst organic compounds many experiments could be arranged to illustrate this point.

The question of the behavior of a current in an electrolyte, also the calculation of the results in chemical equivalents, and mechanical or thermal units, is often considerably complicated by the secondary electrolytic actions (or ordinary chemical reactions), which nearly always occur simultaneously with the electrolytic reactions, and for the proper understanding of all electrolytic phenomena; it is essential, therefore, to regard electrolysis first and comprehensively from the chemical standpoint.

[1] Faraday's nomenclature, dating from 1834.

[2] In this case, however, the hydrogen, simultaneously liberated at the cathode, prevents any rapid action of the HNO_3 on the lead cathode, in which it otherwise is freely soluble, so that solution of the cathode only occurs if we stop the current.

In certain cases, and again at certain temperatures, the secondary reactions are so rapid and complete, as to cause the electrolyte to behave practically as a solid conductor; and it is not impossible that all liquids, which are from experimental observations classed as conductors and not electrolytes, in reality behave in an analogous manner, although the mechanism of such actions cannot at present be traced. A typical case, usefully illustrative of this sort of action, is found in the electrolysis of a solution of a ferrous salt with insoluble electrodes. Iron is deposited at the cathode, and a ferric salt is formed at the anode. But the freshly deposited iron is very soon attacked and dissolved by the rapidly diffusing ferric salt, reforming the ferrous salt, and all in the bath remains *in statu quo*, except that the energy of the current is all converted into heat. This set of reactions may be even more readily illustrated by employing fused lead chloride to which a very small percentage of iron chloride has been added. It is found that the smallest percentage of iron will lower the current efficiency greatly, and with a few per cent only of iron present it will be quite impossible to deposit any lead.

From the chemical standpoint, indeed, many reasons become intelligible which, from the purely electrical standpoint, would be obscure. We can understand, for instance, why certain metals and certain solutions will admit of successful production of metal deposits, whilst others will not; and again, why at certain temperatures, a successful deposit results, and not at other temperatures. Thus, zinc can be produced from its cold sulphate, but not easily from hot sulphate solutions, and not at all from its nitrate solution. Zinc is too rapidly soluble in even the most dilute nitric acid solution to admit of the practical carrying out of any such process. It is soluble only very slowly in cold dilute sulphuric acid solution, but more rapidly as the strength or the temperature of the acid increases, or the surface of the metal becomes roughened. Therefore we shall expect to find (and do actually find in practice) that the process can only be carried on to a certain length in each case, and is dependent on many factors, including the physical state of the surface of the electrodes. Again, aluminium can only with extreme difficulty be produced from its solutions (if at all) and sodium and potassium, etc., practically not at all, so long

as any water is present. In almost every case, when a metal is deposited from a solution, setting free a solvent, a minimum limit to the rate of deposit must be observed, otherwise the deposit ceases; and so on, in many details which will be quite familiar to all practical experimenters.

These limitations are all due to the relative speeds of the electrolysis, and of the secondary reactions. Such metals as potassium and sodium, being rapidly attacked by solutions, or by water, cannot remain in contact with them unchanged, and therefore we find that a minimum ratio of the attack to the speed of deposit is necessary in all cases if any result is to be obtained. In the case of these particular metals, owing to the extreme rate of their attack by any of the solvents of their salts which would be suitable to form electrolytes (even pure water) the minimum rate is away beyond any practical rate of deposit, and the process is at once impossible. In such cases we can, however, have successful recourse to fused electrolytes, to which later reference will be made.

The very simplest form of electrolytic arrangement will serve to illustrate the above described effects.

Fig. 1 represents in diagram a typical electrolytic cell; a bath of liquid, a source of current, an indicator showing the strength and direction of the current, a potential indicator, and two electrodes.

If copper sulphate is the liquid undergoing electrolysis and copper plates the electrodes, the current causes solution of copper at the anode, and a quantitatively corresponding deposit at the cathode; the latter being so constant and determinate as to constitute (with certain precautions taken) a good practical absolute measure of the current flowing during any long period. The electrolyte is not changed, and the potential difference at the electrodes is extremely small, and can be measured solely as a function of the specific resistance according to Ohm's law, plus or minus differences in transfer resistance, etc. If now we substitute a platinum plate for the copper one at the anode — still keeping the current and all other particulars the same — an entirely new set of phenomena appears. Copper is still deposited on the cathode, and still is a direct measure of the current passing, but the radical SO_4 ($SO_3 + O$) is formed and set

free at the anode, and the potential difference at the electrodes is greater by an amount of about one volt. The SO_4 combines with water to form H_2SO_4 which accumulates in the liquid, and one atom of oxygen escapes as gas from the anode. Many other metals, such as zinc, may be deposited from their solutions in such an apparatus. In the case of nearly all, however, after prolonged electrolysis with insoluble anode, the acid will ultimately prevent any further deposit of metal, by accumulating in the liquid bath and redissolving the deposit.

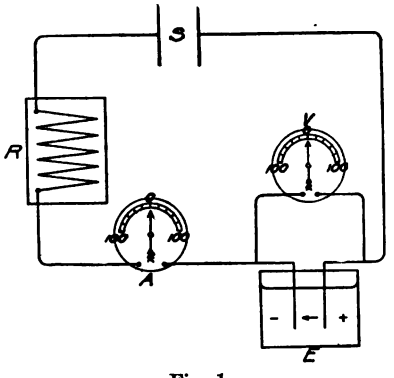


Fig. 1.

If, now, we substitute a solution of common salt and platinum electrodes, a still different set of phenomena will occur. No metal, but an alkali, appears at the cathode, and chlorine gas at the anode; the latter, however, only escapes if produced at a rather rapid rate. The electromotive force, moreover, does not correspond to that known to be necessary for the liberation of sodium and chlorine from salt. The secondary reactions in such a case are as follows: First, chlorine gas and alkali metal are formed at anode and cathode respectively. The alkali metal is immediately attacked by water, forming alkali hydrate and hydrogen gas, which escapes from the cathode. The chlorine partially dissolves in the salt solution. The mingling of chlorine and alkali which soon takes place produces distinctive products according to temperature. Hypochlorite of soda is formed in cold solutions, and chlorate of the alkali metal in solutions over 50° C. Still other conditions will produce perchlorates, and all these compounds mingling in the bath and becoming themselves subject to electrolysis, render this class of reaction somewhat complicated. The details of this particular series are now, however, well known and form the basis of extensive electrochemical industries.

In some processes which have been devised, it has been attempted to take advantage of further secondary reactions by

employing oxidizing substances to combine with the hydrogen which appears at the cathode. This class of action is known as "depolarization," and aims at reduction of total requisite energy. In every case where such secondary reactions occur, the potential difference at the terminals is the sum, or the difference, of that of all the chemical changes taking place *at the surface of the electrodes*, plus the product of the ohmic resistance, and the square of the current flowing, plus or minus the negligible differences of transfer resistance noted. It is to be observed, however, that secondary reactions may freely occur *in the body of the electrolyte* without affecting the voltage or the electrical energy, though they indirectly affect the result. Such reactions are simple chemical changes, and the energy thereof all appears or disappears in the form of heat. Only the changes at the electrodes affect the electrical energy in a direct manner by influencing the electromotive force. This circumstance renders the mathematical formulation of conditions of electrolysis, especially in solutions, still more complicated.

It thus follows that very varying percentages of the total disappearing energy in any bath or apparatus may be employed in actual electrolysis, and varying amounts in the production of heat. If we take the simple case of pure anhydrous zinc chloride which, melted, is a waxlike substance at a temperature of about 420° C., we have an ideal example of a perfect electrolyte. If a current is forced through this medium at high potential (say 100 volts), nearly all (97 per cent) of the energy will be employed in heating the electrolyte, which will rapidly become red hot and ultimately distill. If only 2.2 volts are impressed on the electrodes (and the current may be externally regulated so as to flow at that pressure), extremely little current will pass; nearly the whole of the energy (about 90 per cent) will be employed in electrolysis and only a small residue (10 per cent) in heating. For practically carrying on this process of electrolysis any intermediate voltage may be chosen which, whilst permitting a substantial current, and so bringing about a commercial yield of metal, will also liberate in the melted mass just the requisite quantity of heat to replace that dissipated into the surrounding air by radiation and convection and so maintain the zinc chloride in continual fusion. This will be from 3 to 5 volts, accord-

ing to the size and degree of heat insulation of the apparatus employed.

It thus appears that in every electrolytic process the "total efficiency" of the operation will be less the more rapidly it is carried on, and the greater the ohmic resistance of the apparatus. It therefore arises in practice, that one of the first considerations in all practical designs of electrolytic apparatus is to reduce the ohmic resistance to an economical figure. A second consideration is equally important, although it does not always receive due attention. This is to so arrange the rate of working (current density) that the cost of the energy wasted, as heat, by useless resistance shall have a suitable and stable relation to the capital cost and upkeep of the apparatus. These considerations, which are quite important from a commercial point of view, will be further discussed when dealing with practical methods and designs.[1]

IV.

In media of the third class a variety of phenomena appear which only remotely concern our subject. For the present it may be safely assumed that such phenomena as the fixation of atmospheric nitrogen in the electric arc, the formation of ozone, etc., are temperature effects, pure and simple, and the current, here as in other electrothermal processes, is merely the most convenient source of heat.[2]

Conductors proper are, most generally, of solid form and electrolytes are mostly liquids, whilst gases play only very specialized rôles in the industries we are dealing with; but these conditions are not universal, for both liquid non-electrolytic conductors, and also solid electrolytes are known; thus the electrolysis which occurs in the Nernst lamp filament, when used with continuous currents, is an instance of the latter, and the conduction of mercury, or any fused metal, is an example of the former.

[1] It is a common error amongst scientific men to suppose that the most "efficient" process must be the cheapest. This could be disproved by many examples of commercial practice, but its negation should be self-evident to minds accustomed to think in practical, and not purely academic ways.

[2] In a recent report by S. P. Thompson on the Birkeland-Eyde process, however, this idea is controverted and electrolytic effects are assigned.

Moreover, many fused salts solidify without a perceptible break in their conductivity curves, which seems to indicate that they conduct in the same manner as pure metals.

The most important outcome of the development of electrochemic altheory in its practical bearings is the establishment of the mathematical relations which I shall discuss more fully in the next chapter. The establishment of these relations has had the effect of converting a vague outline, and indistinct body of shadowy ideas, into a sharply defined silhouette of fact; and it now enables us to predetermine nearly every result from any given combination of causes. The first thing necessary to the establishment of such relations is the formulation of a system of units of measurement, connecting mechanical, electrical, thermal, and chemical phenomena; and the discovery of some coincidence laws, or conditions under which such units can be of common application to more than one of these spheres of activities of the forces of nature. Such units have been formulated, and the necessary common ground between the various manifestations of physical force has been found by a series of brilliant observations and deductions, resulting in the formulation of many, now well known, laws some of which have been stated above. I shall discuss the applications of these laws to practical uses in the next chapter.

Meanwhile, to briefly recapitulate, the basis of this elaborate system is the "atomic theory" [1] of elementary chemistry now so firmly established that its truths appear axiomatic. Each element has a given *relative* number called its atomic weight. It also has a given valency, which, however, may vary under different conditions of combination. According to Faraday's law definite quantities of every element (or radical) are always disengaged by a given *quantity* of electricity. The quantity of a substance so disengaged is called the equivalent weight of the element (or radical). The equivalent weights of any substance (either the molecular or the chemical or the electro-chemical equivalents) may be expressed, at pleasure, in grams, or in any other standard

[1] Ostwald, however, has pointed out and adopted the view that proposes to make electrolytic theory independent of the atomic theory. This idea cannot be followed up here, and is not at all essential to a clear understanding of the subject. Refer for further particulars of this idea to "Allgemeine Chemie, etc.," Ostwald.

of weight, by merely calling the relative numbers grams, pounds, tons, etc. The "gram equivalent" is the most useful number for electrochemical calculations; but the use of larger units will be found useful, if systematically practiced, for commercial calculations. In accordance with the nomenclature introduced by Faraday, those substances which appear at the positive terminal of the external circuit receive the name of anions; and those which appear at the negative pole, are called cations. Either are called ions, and the two terminal poles of the electrolytic bath respectively, are the anode and the cathode. The former is that pole at which the current enters the electrolyte, and the latter the pole whence it leaves the bath. It is to be observed, however, that the same elements may be either anions or cations under different conditions of combination. Thus, lead in its combination with chlorine, as lead chloride, is a cation; the metal always appearing at the negative pole. In dilute nitric acid solution, or as a plumbate in caustic soda, however, it becomes an anion; appearing in the form of PbO or PbO_2 (as an acid radical), at the anode or positive pole. The truth of Faraday's law of equivalent weights has never been overthrown, and as long as this law holds good the relations between the quantity of a current and its electrolytic results are absolutely fixed and determinate, and all electrochemical calculation is a matter of the simplest of simple equations. If this were not so there would be no truth in the law of the correlation of the physical forces.

But this does not mean that all electrochemical theories are simple or conclusive; a coincidence law, or an equation, merely takes us back one step, and if we would discover the deep hidden meaning governing such phenomena, we must go back many more. Such retrospect is not at present possible to the human mind, except to a very limited distance. We are in truth merely juggling the cards of a few useful and suggestive coincidences.

To complete this brief sketch of electrochemical theory, it remains to add that the electrochemical phenomena are reversible. The same conditions of contact and decomposition, which demand a given electrical potential difference and a given current for their maintenance, are capable, under certain circumstances (which can be artificially produced), of reversal, maintaining a like potential difference and a like current; such

current is again conditioned by the ohmic resistance. Here, however, the secondary reactions play a most important part, and the feasibility or economy of all primary or secondary galvanic processes is largely conditioned and limited by such reactions.

V.

To account for all observed phenomena in such cases as have been experimentally investigated, many theories have been propounded, but up to the present time few of these can be said to be perfectly satisfactory, though some are decidedly suggestive and useful. The discussion of such theories at length or in great detail can form no proper part of a work like this. Some able and comprehensive text-books on electrochemical theory have recently appeared, and the reader who will pursue the subject further must be referred to these. I may, however, give here, in barest outline, some account of the most modern and widely accepted view of what is known as the *ionic* or *dissociation* theory of electrolytes, in order to indicate the position of the vanguard of scientific opinion on this subject as it stands to-day.

This modern theory of electrolysis rests mainly on the idea of the actual dissociation (or ionization) of the constituents of an electrolyte. The idea was first propounded by Arrhenius from the suggestion of Van't Hoff, on the basis of Pfeffer's experiment; and it has since been greatly elaborated by Ostwald, Ramsay, and others. This theory presupposes that a large number of the molecules in every electrolyte (all, in infinitely dilute solutions, and a lesser number in concentrated ones) are actually in a state of dissociation into ions, each ion existing in its elementary state, but enveloped by a specific charge of electricity which causes it to behave in a different manner to that of similar atoms, or radicals, not so enveloped.

This gigantic assumption which at first sight seems highly improbable, and is certainly not yet a proven fact, nevertheless accounts for many otherwise obscure phenomena. It has therefore, justly, taken a prominent place amongst the provisional theories of science. It was first led up to by observations on the distinctive behavior of electrolytes and non-electrolytes, as regards their osmotic pressures. Certain

substances are electrolytes; that is to say, they can conduct a current of electricity, and suffer decomposition; like, for instance, a solution of zinc chloride, or one of common salt, or the same salts fused. Other substances have not this property, and are termed non-electrolytes. One of these non-electrolytes is a solution of cane sugar. Now a solution of cane sugar behaves towards a body of pure water, under certain highly specialized circumstances, precisely in an analogous manner to the experimentally observed behavior of two gases towards each other under similar circumstances. The osmotic pressure of gases is the pressure set up when two dissimilar gases are separated by a semipermeable membrane; a membrane which has the property — peculiar to some substances — of passing one chemical substance and barring the way to another.

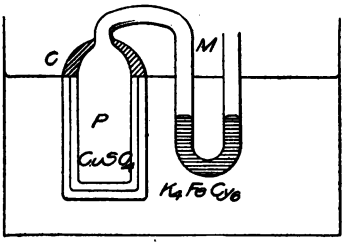


Fig. 2.

To make this clear I will describe the characteristic experiment on which this theory was based, and I cannot better do so than in the words of Arrhenius, the Swedish professor whose lucid and comprehensive treatment of the subject of electrochemical theory is commended to all who will pursue this subject further.

"The experimenter, Pfeffer, filled a porous cylinder, *P* (Fig. 2), with copper sulphate solution, and immersed it in a solution of potassium ferrocyanide. Somewhere about the middle of the cell wall the two solutions met, and there a fine membrane of copper ferrocyanide was formed, which gradually grew stronger. The cell, *P*, whose wall only served as a mechanical support, was washed out, and filled quite full with a solution of cane sugar. A cover, *C*, fitted with a manometer, *M*, was luted on to the cylinder, and the whole apparatus was placed in a water

bath kept at a constant temperature. The water forced itself into the sugar solution, and the pressure in the cell rose to a maximum value, at which evidently water neither diffused into nor out of the cell. The equilibrium was established more quickly when mercury was poured into the open end of the manometer. If the pressure was increased beyond this maximum value, which is the osmotic pressure of the sugar solution in question, water was forced out of the cell into the outer bath."

"Pfeffer first investigated the behavior of solutions of cane sugar of different concentrations, and found the following values:

Percentages of sugar	1	2	2.74	4	6
Osmotic pressure	535	1016	1513	2082	3075 mm. Hg.
$\frac{\text{Osmotic pressure}}{\text{Percentages of sugar.}}$	535	508	554	521	513

The numbers in the last line are very nearly equal, and the differences are easily attributable to the errors of experiment, which are fairly appreciable. The osmotic pressure is, therefore, proportional to the quantity of substance or the number of molecules in unit volume. This corresponds exactly with gas pressure, which, according to the law of Boyle, is inversely proportional to the volume occupied by the gas — that is, directly proportional to the concentration of the gas."

At the very least we have here a truly notable coincidence, and experience has taught the man of science to regard and endeavor to explain such coincidences. The reader who will pursue the fascinating subject of the electrochemical theory further, however, must have recourse to specialized works.

No entirely satisfactory theories have been propounded to account for the action of electricity in the solid conductor, and the accompanying production of heat and absorption of electric potential; the transformation of energy. These phenomena, however, simple as they appear, are really quite as obscure, and as much in need of scientific explanation as the apparently more complex phenomena of electrolytic action. Faraday in the earliest days of electrical discovery attempted to throw some light on this subject, and propounded a doctrine, not yet universally accepted, and in itself somewhat imperfect.

He apparently confused the idea of the correlation of "energy," which has now become an axiom of science, with the much more complex idea of a true correlation of "force," a doctrine which cannot yet be proved.

I will conclude this chapter by a brief mention of the remarkable modern discovery of the "coincidence law" of the periodicity of the chemical elements.

The principles of this periodic theory are now matters of elementary chemical knowledge, and Erdmann's now famous diagram which will be found in his modern text-book on chemistry well illustrates it.

We cannot tell, however, whether the missing elements, necessary to complete the periodic system, will come to us from a more minute study of our own atmosphere like argon, crypton, etc., or whether, like radium, they will come to us as new rare minerals; or, as in the case of didymium, from the breaking down of some other rare element; or, as helium, from a dual source. We cannot tell which (if any) of the several unknown elements may be revealed in the solar spectrum by certain unplaced bands and lines. In the light of modern conceptions who can say, even, whether the whole of our elementary chemical and physical system may not be destined, slowly, to melt away by a rearrangement of its constituent parts, and dreams like those of the old alchemists of the transmutation of metals, become realities; these in their turn to be replaced by greater realities still; even the shadows of which have not yet fallen upon our minds. But it is here that we approach the limits of the human prison house of limitations, and grope blindly against a wall in impenetrable night. Mankind has yet to learn to see with larger eyes the fundamental phenomena and properties of matter and force, and we must probably learn to answer intelligently such questions as "What is matter?" "What is heat?" "What is electricity?" "How does gravitation act?" and other questions of like import, before the gates of our prison house of ignorance, which now bar further passage outwards in all directions, will fall back, and a passage for our understanding be secured to fresh realms of knowledge.

CHAPTER III.

ELECTROCHEMICAL AND ELECTROTHERMAL CALCULATIONS.

I.

THE first thing necessary, in order to make any calculations connecting one form of energy with another, is to establish, by observation and experiment, some common ground, due to observed natural coincidences, and describable by universally applicable laws, or formulæ. The next necessity is to set forth the comparative values of each form of energy in a system of numerical standards or units, and to connect their observed interrelations by equations.

The known forms of energy are mechanical energy, electrical energy, heat, light, and various other forms of radiant energy; only the first three concern our subject at present. Some account of the "coincidence laws" connecting these three forms of energy quantitatively, and the system of units in common use for applying these laws, has been given in the last chapter, and here I shall endeavor to make clear the usual methods of applying these ideas to practical calculations.[1]

The term chemical energy is often used loosely, but in reality the only energy measures of chemical reactions which have yet been quantitatively investigated are the electrical measurements already referred to and the heat liberated or absorbed in chemical combinations or decompositions (reaction). The latter is the province of thermo-chemistry, which again is a

[1] In the c. g. s. (centimeter-gram-second) system of absolute units the dyne is the unit of mechanical force. It is derived from the velocity produced on a given mass (1 gram) in a given time (1 sec.), and it also corresponds with the attraction exerted by the earth at its surface on a mass of $\frac{1}{981}$ gram. The erg is the dyne acting through one centimeter. The kilogram-meter is equal to 9.81×10^7 ergs. It has been determined experimentally that mechanical work equivalent to 42,600 centimeter-grams = 426 gram-meters = .426 kilogram-meter, is required to produce 1 calorie of heat (1 gram of water raised from 15° to 16° C.). Therefore 1 cal. of heat = $9.81 \times 0.426 \times 10^7$

part of the larger subject of thermo-dynamics. But the mechanics (and thermo-dynamics) of corpuscles, atoms, and molecules, is as yet beyond the reach of quantitative investigation, and the only approach to such determinations which we can make is through relative generalizations, such as the atomic theory, — supplemented (in recent years) by the brilliant mathematical flights of men like Helmholz, Clerk-Maxwell, and Lord Kelvin.

Much disinterested and painstaking work has, however, been done in accumulating experimental data in thermo-chemistry. Tables (and critical discussions) of such data are now to be found for nearly all compounds (organic and inorganic), elements, alloys, solutions, etc., in many readily accessible books, amongst which may be mentioned Berthelot's (French) "Thermo Chemie," Ostwald's (German) "Allgemeine Chemie," and Muir's (English) "Elements of Thermal Chemistry." Also in Landholdt and Bernstein's extremely valuable and comprehensive work, "Physikalischen Tabellen," and other works in all languages.

It must be borne in mind that most measurements are made, and these data are usually given, as from the ordinary laboratory temperature (which may be taken at 15° C.); and for all other temperatures the quantities will vary, sometimes quite considerably.

This condition has been productive of some little obscurity in connection with the calculation of critical or theoretical voltages, to which I shall presently refer at some length; for all variations of the critical voltage at varying temperatures seem to indicate a direct transference of energy, from one form to another, without the intervention of an intermediate form (electricity) unless they are exactly proportional to the specific and

$= 0.418 \times 10^8$ ergs. In electrical measurements the unit is the volt-coulomb and 1 volt-coulomb $= \frac{1}{981}$ kilogram-meter $= 0.24$ cal. The values of the practical units expressed in terms of absolute (c. g. s.) electrostatic and electromagnetic units are as follows:

Practical.	Electrostatic.	Electromagnetic.
1 Coulomb	300×10^7	10^{-1}
1 Ampere.	300×10^7	10^{-1}
1 Ohm	$\frac{1}{900} \times 10^{-9}$	10^9
1 Volt	$\frac{1}{3} \times 10^{-2}$	10^8

latent heats involved in the said changes of temperature. Thus the heat of formation of NaCl at 15° C. is 97,600 cal. At its melted temperature (780° C.) it has been experimentally found to be approximately 88,210 cal., and the difference sufficiently closely corresponds to the specific heat of salt (.214) multiplied by 58 grams (one molecule) and by 765° C. (the increase of temperature), to lead us to suppose, both that the latent heat is negligible, and that there is no direct transference of energy to aid the decomposition of salt in this case, without the intervention of electricity. It is probable that there is *never* any such direct transference; but experimental data on this point are meager and insufficient.

We know, however, that most substances manifest great changes in their combining energies, with changes of temperature; and many have entirely different affinities at high temperatures. Such is the case with carbon and calcium, which, both avid for oxygen at ordinary temperatures, will, at the temperature of the carbide furnace (about 3000° C.), reject oxygen and unite together. Again, sodium chloride and other salts in a state of volatilization are, if not actually dissociated, certainly more loosely united than at ordinary temperatures.[1] Some salts like ammonium chloride are known to be dissociated when in a state of volatilization.

A simple rule may now be formulated to connect the "heats of combination," "heats of solution," "latent heats of change of state," etc., for any combination of reagents and their products, at any given temperatures, higher or lower than 15° C., with those contained in the tables. This may be stated thus: "The heat of combination, etc., at $t°$ equals the tabulated heat (at 15°) plus or minus the heat necessary to add or subtract in order to raise or lower the constituents from their ordinary state at 15° C. to their ordinary state at $t°$ C., and plus or minus the heat which would be necessary in order to raise or lower the products from their ordinary state at 15° C. to their ordinary state at $t°$ C." [2]

[1] It is upon such variations in the energy of combination, in fact, that all the older metallurgical and chemical furnace processes, in which electricity plays no part, depend for their efficacy; for the variation range, being different in different materials, renders automatic reactions possible at one temperature which are not possible at another.

[2] J. W. Richards, Met. Calculations.

It is the universal custom to give thermo-chemical data in figures corresponding to a molecular weight of any substance. The atomic weights and molecular weights of the chemical system being merely relative numbers, it is possible to express the weight of the molecule in grams, in kilograms, in pounds, in tons, or in any other unit. Such weights are called gram-molecules, pound-molecules, ton-molecules, etc. The measure of heat used throughout this book is the gram-calorie; therefore all our weights will be expressed as gram-molecules.

When we write the formula expressing the heat of formation of water thus, H_2O = H.F. 69,000 cal., it means that two grams of hydrogen and 16 grams of oxygen = 18 grams (or one gram-molecule) of water, will evolve that quantity of heat, and no more or less in combining; or will demand a similar quantity in separating; the heat being expressed in gram-calories. Again, NaCl = H.F. 97,690 cal., means that 23 grams of sodium and 35.5 grams of chlorine = 58.5 grams (one gram-molecule) of sodium chloride will evolve or demand 97,690 gram-cal. Likewise the molecule of zinc chloride, $ZnCl_2$, weighs 136 grams (65 + 71) and has a heat of formation of 97,400 cal., and the molecule of potassium sulphate weighs 174.2 grams and has a heat of formation of 344,300 cal. The sodium hydrate molecule weighs 40 grams and has a heat of formation of 102,700 cal.

It will be evident, however, that many salts having compound radicals for one or both constituents can be regarded in more than one way from the thermo-chemical standpoint, and will have different heats of formation in each case. It is usual in such cases to indicate by means of a comma or other division of the formula, what precise part or parts of the total combinations the stated figures refer to. A single salt will illustrate this point.

TABLE 1. — THERMO-CHEMICAL DATA OF POTASSIUM SULPHATE.

	M.W.	H. F. — cal.
K_2, S, O_4, Aq.	...	337,700
K_2, S, O_4	174.2	344,300
K_2O, O, SO_2Aq.	...	94,900
K_2SO_3, O	174.2	71,100
K_2O, SO_3Aq.	...	31,400
K_2S, O_4	174.2	240,800
K_2, SO_4	174.2	169,400
K_2, SO_2, O_2	174.2	132,600

Potassium sulphate is made up of seven atoms whose union is capable of being regarded in several different ways. In the above eight examples the commas indicate the point of division of the molecule to which the stated heat refers.

Where commas separate all the constituents of a formula, or when no commas at all are used, it indicates that the total heat of formation of the compound molecule from the individual elementary atoms is expressed.

It will be evident that even in so simple a salt as potassium sulphate the possible division points from the thermo-chemical point of view may be numerous. In some complicated (organic) compound molecules they are almost infinite in number. They, however, are seldom considered except in relation to certain well-known groupings such as bases, acid radicals, or the radicals of bases, alcohols, ketons, aldehydes, etc.

It must always be remembered that for all comparative purposes of energy calculations the valency must also be taken into consideration.

When any of these compounds or salts are formed in the presence of abundance of water, or conversely when they have to be separated from their solutions in abundance of water, a further quantity of heat, called the heat of solution, is evolved, or demanded. Thus, Zn, Cl_2, Aq. corresponds to H.F. 113,000 cal., or 15,600 cal. more than for the fused or solid state, and Na, O, H, Aq., represents H.F. 112,500 cal., or 9800 cal. more than for the solid state. In some cases this heat of solution in water has a negative value. Thus K_2, S, O_4, Aq. gives or demands H.F. 337,700 cal., or 6600 less than K_2, S, O_4., and NaCl, Aq. gives or demands H.F. 97,600 cal., or 1300 cal. less than NaCl. The question of solution heats is, however, still a somewhat obscure one, and the quantitative determinations often vary for every different degree of concentration of a solution, a circumstance which is closely associated with the supposed ionization of solutions, to which reference was made in the last chapter. But this belongs to another subject.

II.

The point at which the science of thermo-chemistry touches those of electro-physics and electro-chemistry, lies in the great generalization known as Faraday's law, to which I referred in the last chapter. This great coincidence law establishes a quantitative relation between the molecular weight (and consequently between the heat of formation) of any substance and the quantity of electricity required for its separation into its elements or radicals.

In order to make this generalization applicable it was necessary to found it on the theory of valencies, thus establishing a new natural constant called the electro-chemical equivalent. This constant is a direct product of the chemical equivalent of the substances concerned and a given quantity of electricity. The chemical equivalent, as we know from elementary chemistry, is related to atomic and molecular weights, by the theory of valencies; for when the atomic weight of an element, or the molecular weight of a salt, is divided by the valency of the element which constitutes the base of the salt, an equivalent weight is obtained which enables all substances to be directly compared to hydrogen as the standard of combining proportions (i.e., makes all equi-valent).

It has been experimentally found that one chemical equivalent in grams of any compound or element corresponds to 96,540 coulombs of electricity. A derived unit is thus established, connecting quantity of electricity with mechanical weight, and it has received the name of the "Faraday." This unit corresponds to 26.87 ampere-hours. That is to say, electricity representing 26.87 ampere-hours (96,540 coulombs), when acting electrolytically, always decomposes a molecular equivalent proportion of every substance and liberates one chemical equivalent in grams of every element or compound radical.

We now have all the elements necessary for calculating the theoretical (or critical) voltage which corresponds to any given heat of combination; for it is evident that, as the current, which is one factor of the energy, has a definite relation to the weight of the liberated elements, the electromotive force which is the other factor of the energy, must also have a definite relation to the same. That is to say, in order to represent a definite num-

ber of joules, or of calories (or of any standard of heat energy), these 96,540 coulombs *must* be delivered at a definite potential. Such is found to be the case.

The value of the critical (or theoretical) electromotive force required to decompose any compound, expressed in volts, is found by dividing the number of calories corresponding to one chemical equivalent of the substance (Q) by 23,040.

The formula may be expressed thus:

$$E = \frac{Q \text{ for one equivalent}}{23{,}040},$$

for $96{,}540 \times .2385$ (joules to calories) $= 23{,}040$.

Or it may be expressed conveniently thus:

$$E = \frac{\text{Mol. weight of salt}}{.24 \times \text{Valency of base}}.$$

It should be noted, however, that this minimum theoretical voltage is not the actual voltage which can be used in practical decompositions and often does not even approximate to it, on account of the tendency, which always exists, to the ready conversion of electrical energy directly into heat energy, in the bath, through the intermediary of ohmic resistance.

It must, moreover, be borne in mind that only the chemical changes occurring at the contact surface of the electrodes[1] with the electrolyte participate in the electrolytic action, and contribute to, or detract from, the voltage. All other chemical changes, occurring in the electrolyte, influence only the sum of the heat, and not the electric potential or the current. Even at the electrodes reactions may occur (local action) due to peculiar conditions of the surfaces or of the electrolyte which do not contribute to, or detract from, the sum of the energy in the external circuit. Such reactions may or may not be electrolytic (due to local circuits, etc.), but it is quite impossible to calculate them, or to consider their results other than as purely chemical phenomena, resulting in heat production. In

[1] I have purposely avoided complicating this explanation by the reference to contact differences of electromotive force occurring between solutions in the same apparatus.

practical processes such local effects are usually avoided by the special design of the apparatus and choice of materials. They therefore play small part in practical calculations and may often be neglected. It is, however, usually due to some such action when the "current efficiency" of any process falls short of the theoretical maximum; and, as is well known, such a shortage actually occurs in nearly every electrolytic process.

A striking advance was made in the science of thermo-chemistry when it was discovered that the heats of formation of all substances, when considered from their elementary state, to a state of dilute solution in water, are *additive*. This means that they are composed of two constant quantities, one being characteristic once for all of the base, and applicable in all its combinations (under like conditions of valency), and the other being similarly characteristic of the acid element or acid radical. There is thus found for each basic element, or each acid, or radical element, or group, a thermo-chemical constant which represents the proportion it contributes to the total energy of formation of any of its compounds. If this constant is expressed in calories for each chemical equivalent, we are able to assign to each element and each radical a definite potential value (in volts or other units), and we can arrange an electric potential series of elements precisely as Bunsen attempted to do many years ago, but with real quantitative values instead of merely relative values.

In a recent communication to the Franklin Institute, Richards[1] has produced the following set of tables of these constants for basic elements, acid elements, and radicals. The tables being mainly for electrical use are given in electro-chemical equivalents and the figures must be multiplied by the number of accents placed against each in order to reduce them to terms of the ordinary molecules.

It must be borne in mind in using these tables that the sum of the constants of any two constituents of a salt gives the heat of formation of that salt, plus its solution in abundance of water; and for fused salts, or concentrated solutions, some correction will always be necessary, the extent of which must usually be determined by experiment.

[1] Electro-chemical Calculations, Journal Franklin Inst., March, 1906. Prof. J. W. Richards.

TABLE 2. — THERMO-CHEMICAL CONSTANTS OF BASIC ELEMENTS.

	Per Chemical Equivalent.	Corresponding Voltage.
	Calories.	
Li	+ 62,900	+ 2.73
Rb	62,000	2.69
K	61,900	2.69
Ba	59,950	2.60
Sr	58,700	2.55
Na	57,200	2.48
Ca	54,400	2.36
Mg	54,300	2.36
Al	40,100	1.74
$(N + H_4)$	33,400	1.45
Mn	24,900	1.08
Zn	17,200	0.75
Fe	10,900	0.47
Cd	9,000	0.39
Co	8,200	0.36
Ni	7,700	0.33
Fe	3,230	0.14
Sn	1,900	0.08
Pb	400	0.02
H	0	0
Tl	− 900	−0.04
Cu	−7,900	−0.34
Hg	−14,250	−0.62
Pt	−19,450	−0.84
Ag	−25,200	−1.10
Au	−30,300	−1.32

TABLE 3. — THERMO-CHEMICAL CONSTANTS OF ACID ELEMENTS.

	Thermo-chemical Equivalent.	Corresponding Voltage.	Salts.
F_2'' (gas)	+52,900	+2.30	Fluoride.
Cl_2'' (gas)	39,400	1.71	Chloride.
Br_2'' (gas)	32,300	1.40	Bromide.
Br (liquid)	28,600	1.20	Bromide.
Br′ (solid)	27,300	1.18	Bromide.
I_2''' (gas)	20,000	0.87	Iodide.
I′ (liquid)	14,600	0.63	Iodide.
I′ (solid)	13,200	0.57	Iodide.
S″ (solid)	− 5,100	−0.22	Sulphide.
Se″ (met.)	−17,900	−0.78	Selenide.

TABLE 4.—THERMO-CHEMICAL CONSTANTS OF ACID RADICALS.

Constituents.	Radical.	Per-chemical Equivalent.	Corresponding Voltage.	Salts.
O_2 (gas) H_2 (gas)	$(OH)'$	+55,200	+2.40	Hydrate.
S (solid) H_2 (gas)	$(SH)'$	3,400	0.15	Sulphydrate.
Se (met) H_2 (gas)	$(SeH)'$	19,100	0.83	Selenhydrate.
Cl_2 (gas) O_2 (gas)	$(ClO)'$	27,500	1.19	Hypochlorite.
Do	$(ClO_3)'$	21,900	0.95	Chlorate.
Do	$(ClO_4)'$	39,400	1.71	Per-chlorate.
Br_2 (gas) O_2 (gas) . . .	$(BrO)'$	28,600	1.24	Hypo-bromite.
Do	$(BrO_3)'$	12,500	0.54	Bromate.
I (gas) O_2 (gas)	$(IO_3)'$	65,000	2.82	Iodate.
Do	(IO_4)	52,600	2.28	Per-iodate.
S (solid) O_2 (gas)	$(S_2O_3)''$	71,750	3.11	Hypo-sulphite.
Do	$(SO_3)''$	75,100	3.26	Sulphite.
H_2 (gas) S (solid) O_2 (gas)	$(HSO_3)'$	149,400	6.48	Bi-sulphite.
Do	$(S_2O_5)''$	115,200	5.00	Pyro-sulphite.
Do	$(SO_4)''$	107,000	4.64	Sulphate.
H_2 (gas) S (solid) O_2 (gas)	$(HSO_4)'$	211,100	9.16	Bi-sulphate.
Do	$(S_2O_8)''$	158,100	6.86	Per-sulphate.
Do	$(S_2O_6)''$	138,500	6.01	Di-thionate.
Do	$(S_3O_6)''$	136,500	5.92	Tri-thionate.
Do	$(S_4O_6)''$	130,600	5.67	Tetra-thionate.
Do	$(S_5O_6)''$	133,100	5.78	Penta-thionate.
Se (solid) O_2 (gas) . . .	(SeO_3)	60,050	2.61	Selenite.
Do	$(SeO_4)''$	72,800	3.16	Selenate.
P (solid) O_2 (gas)	$(PO_4)'''$	99,300	4.31	Phosphate.
H_2 (gas) P (solid) O_2 (gas)	$(HPO_4)''$	152,750	6.63	Mono-H-Phosphate.
Do	$(H_2PO_4)'$	307,700	13.35	Di-H-Phosphate.
As (solid) O_2 (gas) . . .	$(AsO_2)''$	102,150	4.43	Arsenite.
Do	$(AsO_4)'''$	70,200	3.05	Arsenate.
H_2 (gas) As (solid) O_2 (gas)	$(HAsO_4)''$	71,700	3.11	Mono-H-Arsenate.
Do	$(H_2AsO_4)'$	217,200	9.43	Di-H-Arsenate.
N_2 (gas) O_2 (gas)	$(NO_3)'$	48,800	2.12	Nitrate.
Do	$(NO_2)'$	27,000	1.17	Nitrite.
Do	$(NO)'$	−3,800	−0.16	Hypo-nitrite.
C (amor.) O_2 (gas). . . .	$(C_2O_4)''$	99,800	4.33	Oxalate.
Do	$(CO_3)''$	82,450	3.58	Carbonate.
H_2 (gas) C (amor.) O_2 (gas)	$(HCO_3)'$	169,100	7.34	Bi-carbonate.
Do	$(CHO_2)''$	104,600	4.54	Formate.
Do	$(C_2H_3O_2)''$	120,500	5.23	Acetate.
N_2 (gas) C (amor.) O^2 (gas)	$(CNO)'$	37,100	1.61	Cyanate.
C (amor.) N_2 (gas). . . .	$(CNS)'$	−18,100	−0.79	Sulpho-cyanide.
S (solid)	$(CN)'$	−34,900	−1.51	Cyanide.
Fe(solid) C(amor.) N_2 (gas)	$(FeC_6N_6)''$	−25,600	−1.11	Ferro-cyanide.
Do	$(FeC_6N_6)'''$	−52,800	−2.29	Ferric-cyanide.

III.

I shall now consider a few examples, to illustrate the method of applying electrothermal calculations to practical uses. Let it be remembered that all such calculations are a blending of experiment and mathematical deduction, so that for practical uses experiment must always go hand in hand with the use of mathematical generalizations.

A simple process has been devised, let us say for the production of zinc and chlorine, from fused zinc chloride. Amongst other things it is perhaps asserted that the electrolysis can be effected at 3 to 4 volts, also that sodium chloride is mixed in molecular proportion with the zinc chloride, and that it has the effect of increasing the conductivity whilst it is not itself decomposed.

We desire to study this process in detail, with a view to checking the inventors' statements, ascertaining whether it is really a promising method, beforehand, and calculating the power required, the cost, etc.

The first step is to ascertain what reactions actually take place under the conditions proposed, and this is usually best done experimentally in the laboratory on quite a small scale. The small experiment may be supplemented advantageously by a "factory scale" experiment in order to insure that all conditions are the same as they will be in actual practice.

Of course a great deal may be presumed as most likely to occur, and such assumptions will be useful initial starting points to the experimenter; but it will be found a very useful maxim in such investigations to take as little as possible for granted, and also to make all experiments (from the data of which any new piece of apparatus is to be designed) as large and as lifelike as may be consistent with a reasonable scale of costliness. It is only in this way that any real approximation to practical conditions of working can be reached. In the case we are considering the reactions are quite simple. We soon find that zinc chloride being a true electrolyte, and free from secondary reactions (as soon as it is quite free from water), delivers zinc and chlorine in proportions near to the theoretical equivalents for these substances. We also find (experimentally) that the sodium salt, if mixed with the zinc salt, is not decomposed, but yet it substantially reduces the ohmic resistance (probably by reason of a

double decomposition and recomposition occurring, by virtue of which some or all of the current actually travels by way of the better conducting sodium chloride molecules). But the reason of this effect remains somewhat obscure.

To calculate the yield, the consumption, and the minimum theoretical voltage we proceed as follows:

For $ZnCl_2$:

The electro-chemical equivalents in grams per ampere-hour and metric tons per 1000 ampere-years, respectively, are:

	Per Amp.-hr.	*Per 1000 Amp.-yr.*
Zn	1.2195 grams	10.683 tons
Cl_2	1.3220 grams	11.581 tons
$ZnCl_2$	2.5415 grams	22.264 tons

These figures merely require multiplying by the experimentally ascertained current efficiency, say 90 per cent ($\frac{90}{100}$), and the number of apparatus in series, to give the yield of each product and the consumption of electrolyte in the whole plant.

For the voltage:

1 gram-molecule has a heat of formation of 97,400 cal., and the valency of the base (Zn) is 2.

Therefore the theoretical voltage:

$$E = \frac{97{,}400}{98{,}540 \times .2385 \times 2} = 2.1 \text{ volts.}$$

For sodium chloride electro-chemical equivalents as above we have:

	Per Amp.-hr.	*Per 1000 Amp.-yr.*
Na	.85959 gram	7.53 tons
Cl	1.3220 grams	11.585 tons
NaCl	2.18159 grams	19.111 tons

1 gram-molecule has a heat of formation of 97,690 and the valency of the base is 1.

Therefore the theoretical voltage,

$$E = \frac{97{,}690}{96{,}540 \times .2385} = 4.24 \text{ volts.}$$

As the end reactions requiring the least amount of energy will always (with few exceptions) take place, we should conclude

from the above figures that only zinc and not sodium will be deposited, as a final result from the above mixture. Experiment confirms this supposition, and demonstrates that it is practically impossible to obtain any yield of sodium even when the voltage impressed on the electrodes is much above 4.24, so long as any zinc salt remains. (Experiment also yields the information that nearly a full theoretical yield of zinc per ampere-hour is obtained, and we may quite safely write the practical "current efficiency" at 90 per cent.) Further experiments on secondary reactions completely explain the non-ability to deposit sodium and zinc together, from a chemical point of view; for metallic sodium placed in the mixture of fused salts, or in alloy with the fused zinc cathode, will instantly precipitate zinc by simple substitution, and form sodium chloride with much evolution of heat.

So far all is clear, but nothing explains quite definitely why the mere mixture of a salt, which is not finally acted upon at all, will substantially reduce the resistance of the bath and enable a higher current to be passed through it at a lower voltage; in other words, will lessen the conversion of energy by mere heat production in a given sized apparatus. Nevertheless this is found to be the case experimentally in the example under review and in many kindred cases. We can only suppose as above stated that there is a double decomposition and re-formation of the NaCl taking place and that the electrical conductivities of substances have some unknown relation to each other, quite different from their chemical and thermo-chemical relations.

Though we have calculated that 2.1 volts are theoretically required to effect the decomposition, it by no means follows that we can use such a voltage in practice. The actual volts necessary can best be determined by an experiment, on a large enough scale to imitate working conditions in each case (though they may with some accuracy in many cases be calculated from the measured resistance, rate of radiation, specific and latent heats, and other data of the apparatus and the electrolyte). In this case it will be found that at least 2.5 volts must be employed for any practical result, and if the electrolyte is to be kept fused by the current about 3.5 to 7 volts will be necessary according to the perfection of heat insulation employed round the cell and the size of the apparatus. With

very perfect and large apparatus it is possible that 3.0 volts might suffice. An ordinary apparatus for about 1500 amperes requires 5 volts.

For calculating the "total efficiency," we proceed as follows:

In our first experiment we have found that, compared to a standard copper cell put in the same circuit, we obtained 1.1 grams of zinc for each 1.18 grams of copper collected, as against a maximum possible (by Faraday's law) of 1.22 grams. Our current efficiency was, therefore, approximately 90 per cent. The actual electromotive force by experiment was 3 volts.

The electrical efficiency of the process, if employing the lower voltage (with external heating), may now be expressed thus:

(*a*) Amp.-hr. efficiency = 90 per cent.

(*b*) Total " $= \frac{2.1 \times 90}{3.0 \times 100} = 63$ per cent.

When employing a higher voltage (and heating the bath internally) the latter figure (if 5 volts actual are employed) will be:

(*b*) Total efficiency $= \frac{2.1 \times 90}{5.0 \times 100} = 37.8$ per cent.

Though the method of keeping the bath fused by the current is thus shown to be inefficient from a theoretical point of view, there are many cases in which it is *practically* so much more convenient to heat the bath by the current that it will be used in preference to the more *theoretically* perfect method of external heating. For in such cases very special advantages are obtained by the circumstance that, the heating effect being produced *in* the bath, it is not necessary for the melting of the electrolyte that the heat should be transmitted through the walls of the cell. The latter can consequently be constructed of thicker and cheaper material, and in a more permanent way. Also it is *ipso facto* practicable to use a higher current density, and a proportionately smaller apparatus, when working with the higher voltage. In this way the capital cost and interest and depreciation thereon, and the cost of upkeep, are reduced, and these items sometimes bulk very large in the cost sheets of electrolytic works. That is to say, cases exist where

electrical heat is cheaper on application than other sources of heat applied externally in spite of its usually much greater actual cost per heat unit.

From many such considerations I was led long ago to the conclusion that the prevalent method of expressing the "total efficiency" of any electro-chemical operation as the theoretical chemical energy divided by the actual electrical energy, without regard to the heating effect, or to the size or cost of the apparatus, was decidedly deficient in utility, and might be sometimes also very misleading. This is partly because such a method fails to take into account an essential component of every electrolytic process, viz., the energy unavoidably wasted in *uselessly* overcoming natural resistance and dissipated into the surrounding air as heat, or the energy *necessarily* applied as heat to keep the charge and the apparatus at the requisite temperature; and partly also because very important factors which come into the total cost of working, such as the relative size and cost of the apparatus, cannot be so compared at all. When external heat is employed, the relative modes of production by the two systems of working are so different that it is usually still more difficult to make any useful comparison by any mere statement of the "efficiency."

A better system for expressing the relative performance of electrolytic or electro-thermal processes is as follows: First, state the "ampere-hour efficiency," then the "actual volts" employed at each bath or furnace, and from these data and the "1000 ampere-ton-year equivalents" can be easily formulated a figure representing the "yearly product" in tons per kilowatt-year or per horsepower-year of energy expended. Such a figure may be conveniently styled the "kilowatt-year result," or briefly the "result."

This method gives, almost at a glance, the true commercial and chemical "efficiency" for any process, and it is easy in tables to furnish a useful single coefficient for application to the horsepower-year (or kilowatt-year) standard of production, a standard to which all commercial results must be sooner or later referred. The coefficients can be calculated as for one volt and merely multiplied by actual volts in each applied case. Two *commercial* coefficients having this purpose in view have been included in the table of chemical and electro-chemical coefficients at the conclusion of this chapter.

Another example of the application of calculations to practical work may be drawn from some commercial forms of the decomposition of ordinary salt (NaCl) by electrolysis. If this is done in the fused state and metal sodium and chlorine gas produced, the calculation will be on the same lines as the above example ($ZnCl_2$). If, however, it is done in aqueous solution, as is very frequently the case, energy represented by the formation of NaOH from the metallic sodium which is delivered at the cathode must be deducted and allowed for, and so on. When sodium chlorate is the product sought, still greater complications arise in determining the yields and the "total efficiency" of the process, and as usually calculated under these conditions the latter figure becomes of little meaning.

For a caustic soda and chlorine or an $NaClO_3$ process we can calculate as follows:

ELECTROCHEMICAL EQUIVALENTS.

	Grams.	*Tons* (k.w.-year result).
NaCl	2.1859	19.111
NaOH	1.4938	13.085
Cl_2	1.322	11.581
$NaClO_3$	.662	5.8

For the caustic soda process (*a*) the current efficiency experimentally determined may be 80 per cent ($\frac{80}{100}$), and for the $NaClO_3$ process (*b*) it may also be 80 per cent ($\frac{80}{100}$); these numbers multiplied by the above figures and corrected by the addition of any percentage of impurities sold with the finished products, or bought with the raw materials, will give the weight of the products yielded and of the raw materials consumed by employing a given current. In the case of $NaClO_3$ it is to be observed that the equivalent given as the electrochemical equivalent is a figure derived from the chemical process of the various reactions, and not directly from the base of the compound as in the other cases. The reason of this will be clear when it is remembered that $NaClO_3$ is a secondary product (in fact, a tertiary product, or the product of many secondary reactions).

For the minimum electromotive force calculation in these cases we have the following:

(*a*) Critical voltage for decomposition of NaCl = 4.24.[1]

[1] See page 42.

Subtract voltage returned by formation of (2Na, O, H + H_2 from 2Na + $2H_2O$):

$$\frac{112{,}500 - 34{,}500}{96{,}540 \times .2385 \times 2} = 1.69.$$

Difference representing total voltage of reaction = 2.55.

(*b*) A short way of working this reaction out is to consider the end products only, thus:

$$\text{NaCl Aq} + 3H_2O = NaClO_3 + 3H_2.$$

$$-96{,}600 - 207{,}000 + 79{,}200 = \frac{-224{,}400}{6}.$$

Dividing by 6, we have

$$-37{,}400 \text{ cal. per equivalent;}$$

hence, for $E = \frac{-22{,}400}{96{,}540 \times .2385} = -1.62$ volts.

Here the calculated voltage determination has little practical value, for it is a negative quantity, whereas in practice considerable plus voltage is required (several volts per cell) to cause the electricity to flow at the requisite rate and the reactions to take place.

IV.

In many processes it arises that the current is doing more than one kind of chemical work at anode or at cathode or at both. An example of the first is found when a compound anode is dissolving, such as copper silver bullion, and of the latter when an alloy, such as brass, is being deposited at the cathode from a mixed electrolyte of zinc and copper sulphate.

To find the yield, consumption, and theoretical voltage for a given current and mixture in the former case we proceed as follows:

EXAMPLE:[1] In the Wohlwill process of refining gold bullion the anodes consist of 80 per cent gold, 8 per cent silver, 10 per cent copper, and 2 per cent platinum. One hundred and fifty amperes pass through each cell, attacking or corroding the anodes uniformly, while the silver deposits at the bottom of

[1] This example is extracted from Electrochemical Calculations, Richards, 1906.

the bath as AgCl, gold is deposited pure on the cathodes, and platinum and copper accumulate in the solution as $PtCl^4$ and $CuCl^2$ respectively.

REQUIRED: (1) How much weight of anode is corroded per twenty-four hours?

(2) How much more gold is deposited than is dissolved?

(3) What voltage of decomposition, to represent chemical work, must be furnished?

SOLUTION: (1) One kilogram of anode contains:

Gold	800 grams
Silver	80 "
Copper	100 "
Platinum	20 "

The coulombs necessary to dissolve these weights and to convert these metals into $AuCl^3$, AgCl, $CuCl^2$ and $PtCl^4$ are :

		Coulombs.
Gold	$800 \div (0.00001035 \times 197 \div 3) =$	1,177,076
Silver	$80 \div (0.00001035 \times 108 \div 1) =$	71,570
Copper	$100 \div (0.00001035 \times 63.6 \div 2) =$	303,831
Platinum	$20 \div (0.00001035 \times 195 \div 4) =$	39,638
		1,592,115

Coulombs available, per 24 hours :

$$150 \times 60 \times 60 \times 24 = 12{,}970{,}000.$$

Anode corroded away in 24 hours, per cell :

$$12{,}970{,}000 \div 1{,}592{,}115 = 8.146 \text{ kilograms}$$
$$= 8{,}146 \text{ grams} \qquad (1)$$

(2) The weight of gold deposited, by the total current is :

	Grams.
$12{,}970{,}000 \times (0.00001035 \times 197 \div 3) =$	8,815
Amount dissolved, $8{,}146 \times 0.80 =$	6,717
Shortage in each cell, per 24 hours =	2,098 (2)

This shortage, it will be recalled, has to be made up by dissolving some of the bullion in acid, and adding it to the cells. There would be required $2{,}098 \div 0.80 = 2{,}747$ grams of bullion

thus dissolved, making the total bullion treated per cell per day 8,146 + 2,747 = 10,893 grams, of which 8,146 grams, or 74.8 per cent, would be treated electrolytically in the cell, and the rest, 25.2 per cent, would be dissolved chemically, and yet when added to the electrolyte, its gold deposited electrically.

(3) Basing calculations on the solution of a kilogram of anode, requiring the passage of 1,592,115 coulombs (16.49 faradays), the 800 grams of gold dissolved have a corresponding 800 grams deposited, so that no chemical energy needs to be expended for it. For the other elements we have the following equations and heat absorptions or evolutions:

$$\begin{aligned} &AuCl^3, Aq + 3Ag = Au + 3AgCl. \\ &-27{,}200 \qquad\quad + 3\,(29{,}000) = +\ 59{,}800 \text{ cal.} \\ &2AuCl^3, -Aq + 3Cu = 2Au + 3CuCl\ 2Aq. \\ &-2\,(27{,}000) \qquad\quad + 3\,(62{,}500) = +\ 133{,}500 \text{ cal.} \\ &4AuCl^3, Aq + 3Pt = 4Au + 3PtCl^4Aq. \\ &-4\,(27{,}000) \qquad\quad + 3\,(79{,}800) = +\ 131{,}400 \text{ cal.} \end{aligned}$$

The above heat evolutions are for the solution of, respectively,

3 gram atomic weights of silver = 324 grams.
3 gram atomic weights of copper = 190.8 grams.
3 gram atomic weights of platinum = 585.0 grams.

The heat evolution per kilogram of anode corroded will therefore be for:

$$\begin{aligned} \text{80 grains silver} &= \frac{80}{324} \times 59{,}800 = 14{,}765 \text{ cal.} \\ \text{100 grains copper} &= \frac{100}{190.8} \times 133{,}500 = 69{,}980 \text{ cal.} \\ \text{20 grains platinum} &= \frac{20}{585} \times 131{,}400 = 450 \text{ cal.} \end{aligned}$$

Sum = 85,195 cal.

This heat evolution takes place for the passage of 1,592,115 coulombs (16.46 faradays). For one faraday (96,540 coulombs) it will be:

$$85{,}195 \div 16.49 = 5{,}167 \text{ cal.};$$

and since one faraday falling in potential one volt represents 23,040 cal., the heat evolution will generate

$$5{,}167 \div 23{,}040 = 0.224 \text{ volt},$$

which means that the fall of potential for chemical work is negative, i.e.,

$$E_d = -\ 0.224 \text{ volt}. \tag{3}$$

It is interesting to note that, the observed total drop of potential across the baths being 0.7 volt, the voltage drop to overcome ohmic resistance must be greater than this, i.e.,

$$\begin{aligned} E &= E_d + E_c \\ 0.7 &= -\ 0.224 + E_c \\ E_c &= 0.7 + 0.224 = 0.924 \text{ volt}, \end{aligned}$$

making the ohmic resistance of the cell

$$\begin{aligned} R = \frac{0.924}{150} &= 0.00616 \text{ ohm} \\ &= 6.16 \text{ milli-ohms}. \end{aligned}$$

Further, if no external source of current were used, the cell would have available 0.224 volt electromotive force, which should, if short circuited, send

$$\frac{0.224}{0.00616} = 36.3 \text{ amperes}$$

through the bath, that is, run it at 24 per cent of the present rate, without any external generator or current.

To find the voltage required for mixed electrolysis we proceed as follows:

EXAMPLE:[1] An electrolyte contains zinc sulphate with some copper sulphate, and is electrolyzed with a copper anode. There is deposited upon the cathode in one hour 15 grams of brass, containing one-third zinc and two-thirds copper. What voltage drop will occur in the cell in addition to that necessary to overcome its ohmic resistance?

[1] This example is extracted from Electrochemical Calculations Journal, Franklin Inst., Richards, 1906.

SOLUTION: The coulombs passing are those necessary to deposit 5 grams of zinc (chemical equivalent $65 \div 2$) and 2 grams of copper (chemical equivalent $63.6 \div 2$).

$$\text{Coulombs for zinc} = \frac{5.0000}{0.00001035 \times (65 \div 2)} = 14{,}864$$

$$\text{Coulombs for copper} = \frac{10.0000}{0.00001035 \times (63.6 \div 2)} = 30{,}383$$

$$\text{Sum} = 45{,}247$$

The weight of copper dissolved will be, on the same principles:

$$45{,}247 \times 0.00001035 \times (63.6 \div 2) = 14{,}892 \text{ grams.}$$

The solution of 14,892 grams of copper and deposition of 10 grams of the same element, shows that the only thermo-chemical energy required is that absorbed for the solution of 4.892 grams of copper and deposition, therefore, of 5.0 grams of zinc. The thermo-chemical equation is:

$$ZnSO^4Aq + Cu = CuSO^4Aq + Zn$$
$$-248{,}000 \qquad +197{,}500 = -50{,}500 \text{ calories,}$$

showing that 50,500 calories are absorbed for every 65 grams of zinc (its atomic weight) thus deposited. This equals an absorption of 3,885 calories per 5 grams of zinc, or for the whole period during which 45,247 coulombs passed through the cell. For every 96,540 coulombs passing, the thermo-chemical heat absorption is

$$\frac{3{,}885}{45{,}247} \times 96{,}540 = 8{,}289 \text{ calories,}$$

and the voltage drop is

$$E_d = \frac{8{,}289}{23{,}040} = 0.36 \text{ volt.}$$

The above calculation is on the assumption that the copper and zinc deposit separately, as mixed crystals. If they really deposit as a chemical combination, the heat of formation of the alloy would need to be considered also.

V.

When only the thermal effect of the current has to be considered, practical calculations are also often required to determine what temperatures and what other results can be attained to with a given energy. As the rate of heat radiation from a furnace is dependent on many indeterminate conditions, and also varies greatly with the temperature, it will usually be found most practical to determine such questions of radiation or convection losses as usually arise, largely by experiment.

In all cases, however, a balance sheet of the thermal energy of the reactions and of the end products can be advantageously drawn up. The heating power of any given current may be calculated according to the formula H (cal. per sec.) $= C^2$ (amp.) $\times R$ (ohms) $\times .24$ (joules to cals.) plus or minus the absorption, or liberation, of heat energy, corresponding to the chemical reactions occurring, and the specific heats, latent heats, etc., of the raw materials, wastes, and finished products.

The resistance of a furnace or bath is not often accurately known beforehand, but may be postulated with accuracy from the experimentally determined electromotive force and the known current.

EXAMPLE: A furnace takes 8,000 amperes and 50 volts at the terminals. The resistance of the furnace hot is therefore $\frac{50}{8000} = .00625$ ohm.

The total heat generated in one second is

$$64{,}000{,}000 \times .00625 \times .24 = 96{,}000 \text{ cal.}$$

For each hour the amount will be 3,600 times as great and so on.

To determine the effect of this quantity of heat on any given charge of materials which in themselves undergo many changes of temperature, state, and combination is manifestly a complicated problem; and it is further influenced by the rates at which radiation, conduction, and convection are going on. Such problems can, however, be attacked step by step, and with the aid of more or less approximate experimental generalizations.

For illustrations of the method of conducting the calculations relating to purely chemical changes I quote another excellent example from the treatise already referred to:[1]

"If the thermo-chemical problem involves the simultaneous

[1] Met. Calculations. J. W. Richards, 1906.

decomposition of one or more substances, and the formation of one or more others, then the chemical equation should be written, and a thermo-chemical interpretation given of all the energy involved in the passage from starting compounds to products. Every chemical equation can be thus interpreted, if the heats of formation of all the compounds represented in it are known. We obtain the net energy of the reaction by assuming that all the substances used are resolved into their elements, and that all the products are formed from their elements; the first item is, therefore, to add together the heats of formation of all the substances used, starting with their elements, and by changing the algebraic sign of this sum we have the heat necessary to decompose the substances used into their elements; the second item is similarly found by adding together the heats of formation of all the substances formed; the difference between these two items is the net energy of the reaction. In making these summations, regard must, of course, be paid to the number of molecules of each substance concerned, as shown in the reaction; because the tabulated data are the heats of formation of one molecule only, and to the algebraic sign of the heats of formation.

"EXAMPLES: (*a*) What heat is evolved when dry ferric oxide is reduced by aluminium, in the Goldschmidt "Thermit" process?

$$\begin{array}{l} Fe^2O^3 + 2Al = Al^2O^3 + 2Fe \\ \quad -195{,}600 \quad +392{,}600 \\ \hline \textit{Ans.} \quad +197{,}000 \text{ cals.} \end{array}$$

"(*b*) Write the equation showing the reaction of metallic sodium in water in excess :

$$\begin{array}{l} 2H^2O + 2Na = 2NaOH + 2H + \text{Aq. (excess water)} \\ -2\,(69{,}000) + 2\,(112{,}500) \\ \hline \quad -138{,}000 + 225{,}000 \\ \hline \textit{Ans.} \quad +87{,}000 \text{ cals.} \end{array}$$

"(*c*) What heat is evolved in the reaction of water on calcium carbide to form acetylene gas?

$$\begin{array}{l} CaC^2 + 2H^2O = CaO^2H^2 + C^2H^2 \\ -(-6{,}250) - 138{,}000 + 215{,}600 + (-54{,}750) \\ \hline \quad -131{,}750 + 160{,}850 \\ \hline \quad \textit{Ans.} \quad +29{,}100. \end{array}$$



"The last case leaves out the very small heat of solution of the calcium hydrate, which would normally go into solution. If such a large excess of water was used that all the calcium hydrate formed could dissolve, the heat of formation of the hydrate in dilute solution, 219,500 cals., would be used, and the final result would be 33,000 cals. The case is also very instructive, because it contains two compounds which are endothermic, that is, their heat of formation is negative, and, therefore, as in the case of CaC^2, heat is given out when it decomposes, while in the case of C^2H^2 heat is absorbed when it is formed."

This must conclude my review of chemical and electrical calculations. For those who would follow this most fascinating branch of practical mathematics further no better aid can be recommended than the work of Prof. Richards, from which I have quoted.

For an example of the methods which have sometimes been adopted for calculating radiation problems from purely mathematical data, reference is made to the works of Clerk-Maxwell and others. A recent paper[1] read by C. L. Collins at the Cornell meeting of the American Electro-chemical Society, dealing specially with radiation problems applied to the carborundum furnace, is also of some interest.

It is manifest that this subject of the application of mathematics to the science we are dealing with is worthy of a much more exhaustive treatment than can possibly be given to it in the space at disposal in a treatise of this description. It has been my aim therefore to be suggestive and stimulating in my treatment of it, rather than exhaustive; and the same remark will hold good practically throughout this book, which deals, in a general manner, with an immense variety of highly specialized subjects, each often worthy of a treatise to itself.

VI.

The table which follows is a fitting conclusion to this chapter. Departing slightly from the usual custom followed in preparing such tables, the constants calculated have been separated into three departments: (1) chemical; (2) electro-chemical; (3) com-

[1] Some Principles of Furnace Design. From Am. Elec. Chem. Soc., Vol. 9, p. 31.

mercial. The first two departments do not call for special comment. The figures in these divisions of the table have been made comprehensive and brought up to date, and are corrected from the latest determinations and the best sources of information available. Division (3) contains two columns of constants of purely commercial utility. As I have remarked above, it usually arises in all commercial calculations and estimates that the percentage of "current efficiency" and the actual measured voltage at the poles of each bath, or apparatus (often experimentally determined), are the data known beforehand. The constants here given are the calculated "result" or yield of any element in metric-tons per kilowatt-year, and per electrical horsepower-year respectively, assuming a current efficiency of 100 per cent and an electromotive force of one volt, at each apparatus. A very simple calculation with these constants will give the actual yields to be expected from any given source of power or any given process.

TABLE 5. — CONSTANTS OF THE ELEMENTS.

Name of Elements.	Symbol.	Valency.	Chemical Constants.		Electro-Chemical Constants.			Commercial Constants. "Result."	
			Atomic Weights.	Chemical Equivalents.	Per Coulomb (i.e. per amp. sec.) in mg. per sec.	Per Ampere hour (i.e. 3600 Coulomb) in grams	Per Faraday (i.e. 96540 Coulomb) in grams.	Per 1000 Ampere years (i.e. 8760 hrs.) in met. tons.	Per Horse-p. year for one volt in metric tons.
Aluminium .	Al	III	27.10	9.03	.09354	.33674	9.033	2.950	2.201
Antimony .	Sb	III	120.20	40.07	.41509	1.4943	40.067	13.090	9.765
Argon . . .	A	*	39.9	...	...	...	...	...	...
Arsenic . .	As	III	75.00	25.00	.25898	.93233	25.000	8.167	6.093
Barium . .	Ba	II	137.40	68.70	.71166	2.5620	68.700	22.443	16.742
Beryllium. .	Be	II	9.1	4.55	.04713	.16967	4.550	...	...
Bismuth . .	Bi	III	208.50	69.50	.71995	2.5918	69.500	22.704	16.937
Boron . . .	B	III	11.00	3.67	.037800	.13608	3.667	1.192	0.8892
Bromine . .	Br	I	79.96	79.96	.82831	2.9819	79.960	26.221	19.561
Cadmium .	Cd	II	112.40	56.20	.59229	2.1322	56.200	18.678	13.934
Cæsium . .	Cs	I	132.9	132.9	1.37671	4.9562	132.900	...	...
Calcium . .	Ca	II	40.10	20.05	.20770	.74772	20.050	6.550	4.886
Carbon . .	C	IV	12.00	3.00	.031077	.11188	3.000	.9801	.7311
Cerium . .	Ce	III	140.25	46.75	.48428	1.7434	46.750	...	...
Chlorine . .	Cl	I	35.45	35.45	.36723	1.3220	35.450	11.581	8.639
Chromium .	Cr	II	52.10	26.05	.26985	.97146	26.050	8.510	6.348
	Cr	III	52.10	17.37	.17994	.64778	17.367	5.677	4.235
Cobalt . . .	Co	II	59.00	29.50	.30559	1.1001	29.500	9.637	7.189
	Co	III	59.00	16.67	.20376	.73354	19.667	6.426	4.794

TABLE 5. — *Continued.*

Name of Elements.	Symbol.	Valency.	Chemical Constants.		Electro-Chemical Constants.			Commercial Constants. "Result."	
			Atomic Weights.	Chemical Equivalents.	Per Coulomb (i.e. per amp. sec.) in mg. per sec.	Per Ampere hour (i.e. 3600 Coulomb) in grams.	Per Faraday 96540 (i.e. Coulomb) in grams.	Per 1000 Ampere years (i.e. 8760 hrs.) in met. tons.	Per Horse-p. year for one volt in metric tons
Copper . . .	Cu	I	63.60	63.60	.65883	2.3718	63.600	20.777	15.500
	Cu	II	63.60	31.80	.32942	1.1859	31.800	10.388	7.749
Erbium. . .	Er	III	166.	55.33	.57316	2.0634	55.333	...	...
Fluorine . .	F	I	19.00	19.00	.19682	.70855	19.000	6.207	4.630
Gadolinium .	Gd	III	156.	52.00	.53867	1.9392	52.000	...	...
Gallium . .	Ga	III	70.	23.33	.24168	.87005	23.333	...	...
Germanium .	Ge	IV	72.5	18.13	.18781	.67612	18.125	...	...
Gold	Au	III	197.20	65.73	.68090	2.4512	65.733	21.473	16.019
Helium . .	He	*	4.0	...	...	...	...	...	...
Hydrogen. .	H	I	1.008	1.008	.010442	.037591	1.008	.3293	.2456
Indium . .	In	III	115.	38.33	.39706	1.4294	38.333	...	...
Iodine . . .	I	I	126.97	126.97	1.3153	4.7351	126.970	41.479	30.943
Iridium. . .	Ir	IV	193.0	48.25	.49982	1.7993	48.250	...	...
Iron	Fe	II	55.90	27.95	.28953	1.0423	27.950	9.131	6.812
	Fe	III	55.90	18.63	.19279	.69404	18.633	6.090	4.543
Krypton . .	Kr	*	81.8	...	...	...	...	...	...
Lanthanum .	La	III	138.9	46.30	.47962	1.7266	46.300	...	...
Lead . . .	Pb	II	206.9	103.45	1.07164	3.8579	103.450	33.795	25.211
Lithium . .	Li	I	7.03	7.03	.07282	.26215	7.030	2.297	1.714
Magnesium .	Mg	II	24.36	12.18	.12617	.45422	12.180	3.979	2.968
Manganese .	Mn	II	55.00	27.50	.28587	1.0291	27.500	9.015	6.725
	Mn	III	55.00	18.33	.18988	.68357	18.333	5.988	4.467
Mercury . .	Hg	I	200.00	200.00	2.0718	7.4585	200.000	65.333	48.738
	Hg	II	200.00	100.00	1.0359	3.7292	100.000	32.667	24.370
Molybdenum	Mo	II	96.00	48.00	.49723	1.7900	48.000	15.680	11.697
Neodymium.	Nd	III	143.6	47.87	.49589	1.7852	47.867	...	...
Neon . . .	Ne	*	20.	...	...	...	...	...	...
Nickel . . .	Ni	II	58.70	29.35	.30404	1.0945	29.350	9.588	7.153
	Ni	III	58.70	19.57	.20273	.72983	19.567	6.393	4.769
Niobium . . (Columbium)	Nb Cb Ko	III	94.	31.33	.32455	1.1684	31.333	...	...
Nitrogen . .	N	III	14.04	4.680	.048480	.17453	4.680	1.529	1.141
Osmium . .	Os	IV	191.	47.75	.49464	1.7807	47.750	...	...
Oxygen. . .	O	II	16.000	8.000	.082872	.29834	8.000	2.613	1.949
Palladium .	Pd	II	106.5	53.25	.55162	1.9858	53.250	17.396	12.977
Platinum . .	Pt	IV	194.80	48.70	.50448	1.8161	48.700	15.909	11.868
Phosphorus .	P	V	31.00	6.20	.064226	.23121	6.200	2.025	1.511
Potassium .	K	I	39.15	39.15	.40555	1.4600	39.150	12.790	9.541
Praseodymium	Pr	III	140.5	46.83	.48511	1.7464	46.833	...	...
Radium . .	Ra	...	225.	...	...	...	...	...	...
Rhodium . .	Rh	III	103.0	34.33	.35562	1.2802	34.333	...	...
Rubidium .	Rb	I	85.5	85.5	.88569	3.1885	85.500	...	...
Ruthenium .	Ru	IV	101.7	25.43	.26343	.94835	25.425	...	...
Samarium .	Sm	III	150.3	50.10	.51899	1.8684	50.100	...	...
Scandium .	Sc	III	44.1	14.70	15228	.54821	14.700	...	...

TABLE 5. — *Continued.*

Name of Elements.	Symbol.	Valency.	Chemical Constants.		Electro-Chemical Constants.			Commercial Constants. "Result."	
			Atomic Weights.	Chemical Equivalents.	Per Coulomb (i.e. per amp. sec.) in mg. per sec.	Per Ampere hour (i.e. 3600 Coulomb) in grams.	Per Faraday 96540 (i.e. Coulomb) in grams.	Per 1000 Ampere years (i.e. 8760 hrs. in met. tons.	Per Horse-p. year for one volt in metric tons.
Selenium . .	Se	IV	79.2	19.80	.20511	.73840	19.800	...	...
Silicon . . .	Si	IV	28.40	7.10	.073549	.26478	7.100	2.319	1.730
Silver . . .	Ag	I	107.93	107.93	1.11805	4.02498	107.930	35.267	26.309
Sodium . .	Na	I	23.05	23.05	.238775	.859590	23.050	7.530	5.617
Strontium .	Sr	II	87.60	43.80	.45372	1.6334	43.800	14.309	10.675
Sulphur . .	S	II	32.06	16.03	.16605	.59778	16.030	5.237	3.907
Tantalum .	Ta	V	183.	36.6	.37914	1.3649	36.600	...	...
Tellurium. .	Te	IV	127.6	31.9	.33045	1.1896	31.900	...	...
Terbium . .	Tb	III	160.	53.33	.55245	1.9888	53.333	...	...
Thallium . .	Tl	II	204.1	102.05	1.05714	3.8057	102.050	33.338	24.870
Thorium . .	Th	IV	232.5	58.13	.60217	2.1678	58.125	...	...
Thulium . .	Tm	III	171.	57.00	.59046	2.1257	57.000	...	...
Tin	Tn	II	119.00	59.5	.61636	2.2189	59.500	19.438	14.501
	Tn	IV	119.00	29.75	.30818	1.1094	29.750	9.718	7.250
Titanium . .	Ti	IV	48.1	12.03	.12462	.44863	12.025	3.930	2.932
Tungsten . .	W	II	184.	92.00	.95303	3.4309	92.000	30.055	22.421
	W	III	184.	61.33	.63532	2.2872	61.333	20.036	14.947
	W	VI	184.	30.67	.31771	1.1438	...	10.020	7.475
Uranium . .	U	IV	238.5	59.63	.61771	2.2238	59.625	19.480	14.532
Vanadium .	V	V	51.2	10.24	.10608	.38171	10.240	3.346	2.496
Xenon . . .	Xe	*	128.	...	...	...	...	...	...
Ytterbium .	Yb	III	173.0	57.67	.59740	2.1506	57.667	...	...
Yttrium . .	Yt	III	89.0	29.67	.30735	1.1065	29.667	...	...
Zinc . . .	Zn	II	65.40	32.70	.33874	1.2195	32.700	10.683	7.970
Zirconium .	Zr	IV	90.60	22.65	.23463	.8447	22.650	7.400	5.520

CHAPTER IV.

VALUE OF ELECTROCHEMICAL AND ELECTROTHERMAL PROCESSES.

THE market price of products, the cost of raw materials, the percentage of recoveries and the cost of operating, are the four essential factors in all commercial calculations relating to electrolytic or electro-thermal processes. A factor also of great importance is the capital involved in the necessary works, tools, and outfit; for such capital must often be invested at considerable risk of loss (especially from market fluctuations) and so must be sometimes valued at almost speculative rate. In projecting new enterprises it is especially necessary to consider the stability of the market which exists for any proposed product, and how far increased output is likely to affect prices.

Charges on capital, such as interest on the capital locked up (if such capital is raised by bonds or debenture loans), together with a charge for depreciation or amortization of plant, and sinking funds for redemption of loans, must all be added to the actual operating expenses, in order to arrive at the real cost of any process of production; and as such works are, by experience, frequently changing, and giving place to new methods — changes which often necessitate entirely new machinery every few years — it is often necessary to fix the amortization charges somewhat high.

The life of few electro-chemical or metallurgical, special apparatus can be safely computed at more than seven or eight years; therefore it is necessary to allow about 10 per cent of the cost of such apparatus as a yearly charge for this purpose. The amortization on such plant as power machinery and works buildings, however, may be lower, especially if the basic conditions offered in modern times by good water powers, equipped with first-class, up-to-date machinery and housings, have been selected in the first instance; for there does not seem to be any reasonable probability that

such plant can either become obsolete, or be worn out in less than twenty years; whilst the degree of total efficiency already obtained (viz., some 95 per cent for the dynamos and 80 per cent for good turbines) does not leave much margin for possible future improvements, necessitating new apparatus. For such apparatus, therefore, an amortization charge of 5 per cent yearly, computed on the actual cost, is sufficient.

There can be no question about the propriety of entering up these capital charges;[1] the only question is as to their exact amounts. For all except quite unusual circumstances the above rates will prove reliable.

The question of interest on capital is, however, on a rather different footing from the other capital charges, for it may fairly be argued that all interest is more properly merged in profits, and comes out in the dividends ultimately to be earned from a given investment of capital; and therefore interest should form no part of the calculation of costs. This, however, is merely a matter of bookkeeping, and its importance is not great, so long as clear ideas are entertained as to what is meant by any statement of costs or profits. Throughout this book I do not include any "interest" on capital, in any statement of costs, unless such charge is clearly specified, and for a specific reason, as in the case of debenture interest, which of course forms a proper charge against costs. Ample depreciation rates and also redemption fund allowances are included in all cases in the calculations.

After the capital charges have been disposed of, the other items of cost will vary in different manufactures in their relative importance. The order is usually somewhat as follows:

1. Energy.
2. Labor.
3. Raw material.
4. Packing finished products.
5. Upkeep (meaning specific renewals and repairs, not general deteriorations).

[1] In addition to interest on borrowed capital, and depreciation of various grades on plant, if an undertaking is to be financially sound, a sinking or redemption fund must also be created by a yearly charge on profits. For this purpose (which theoretically contemplates the complete extinction of the industry and so provides for the return of the entire capital at the end of the redemption period), a charge ranging from 2½ per cent to 5 per cent of the gross capital employed will be sufficient for most stable industries.

6. Freight on raw material from markets to works.
7. Freight on finished products to markets from works.
8. Management and office expenses.
9. Selling expenses and commission.
10. Rents, rates, taxes, and insurance.

The proportion of the value of the raw material as against the other items of cost will, however, of course vary greatly in different industries. Against these ten items of cost, plus properly calculated capital charges, the gross market value of all the yearly products of any works may be placed, and the difference will represent the net profit or loss on the operation of the factory.

The site for such operations must be chosen after duly weighing the relative costs of such items as energy; freights on the raw materials and finished products; import duties, and labor. A balance sheet may readily be produced on the basis of known data (assisted by experiment where any novelty in the operations is involved) which will give a sufficiently accurate forecast of the result to be expected from any given scale of operations at any chosen site.

This is seemingly very simple, and with proper care and a sufficient amount of judicious experiment to determine beforehand the percentage of recoveries, and each item of working cost, there ought not to be (and in fact seldom is) any insurmountable difficulty in arriving beforehand at a very close, if not completely accurate, estimate of the balance of profit obtainable and the amount of capital required to supply any given product at a fixed market price.

It would seem at first sight, therefore, somewhat surprising that so much timidity on the part of capital exists, or that in actual commercial experience so much capital has been unprofitably expended in unfruitful works. (And this quite apart from legitimate experimenting with a view of improved methods; the cost of the latter being always indeterminate must be specially dealt with.) By far the greatest practical difficulty in all commercial enterprises, however, is presented by the enormous fluctuations of market values of products which periodically occur, and the necessity for foresight which such fluctuations involve.

Such difficulties are inherent to all business enterprises, and hitherto any attempts to remove this difficulty (under which all

commerce labors) by regulating prices through various forms of legislation, has not proved successful. We are here face to face with the workings of natural laws of supply and demand. Human skill has not yet been able to grapple with and regulate such forces, and it is not a little curious to the thoughtful mind to note that so few of the many people who follow commercial occupations realize how similar the risks which they daily must run in their occupations, are with the risks taken by any speculator in uncertain values. No commercial enterprise can, in truth, be free from the speculative element. The people who follow old-fashioned business conventions, wedded to conservative business ideals, and believing that they are encouraging only a highly moral and perfectly safe policy in the investment of their capital, are in truth often exposed to greater risks than the mere stock exchange gambler, — greater because they are unseen. Even farmers must gamble in weather. In fact the ultra-conservative ideal of perfect solidity and certainty in business matters is a pleasant fiction, not a reality under mundane conditions of industry.

It sometimes seems to me to be due to the greater grasp of this fundamental fact which Americans have attained, either consciously or unconsciously, that so much American industrial success has resulted. For a nation or an individual who realizes that speculation, in some form or other, is not only not blameworthy, but is often a necessary condition for successful business, will not be unduly hampered by conventional, and often wholly impractical, ideals of security; but will have the mind and intelligence free to develop the only real safeguard of property, which is individual judgment compounded of intelligence and resourcefulness. I am convinced that many of the conditions of commerce in America, which more conservative nations, like England, regard as dangerous and reckless, have been in truth praiseworthy, in as far as they have encouraged freer enterprise (of course not in as far as they promote dishonest practices which unfortunately often go hand in hand in such matters). A loss of capital under such conditions, however regrettable it may be, will not be quite so paralyzing and destructive of further effort as it is under the more conservative conditions prevailing in an older country; for the man who loses his capital and so is down to-day, when money is freely circulating, may the more easily regain it and so be up to-morrow if he has energy and pluck.

Such conditions nearly always rule in a new country; and it is well known that the older countries have continually to look to new countries, with their greater producing power and freedom from ultra-conservatism, for an outlet for their energies.

No one who knows anything of the necessities and the pitfalls of practical work, however, will quarrel with the business man whose desire is to make his results as sure and as free from surprises as possible. The three elements he has to eliminate to the utmost in order to promote this result, as every business man knows, are experiment, extravagance, and fraud. The latter two are matters of ordinary business precaution and do not specially concern us here. I may say, however, with regard to real and false economies, that this also is largely a matter for individual judgment. For whilst economy in every direction is the very first principle necessary to success, and systematic extravagance in any commercial enterprise, in nine cases out of ten will spell failure; yet there are many apparent extravagances which are true economies, and vice versa. It is frequently a matter of experience that the office man's view of true economy will not be the works man's view and so on. Only the capacity for individual judgment can be of any comprehensive service in deciding or criticising such matters, and it is a good maxim to be guided in one's judgment of other people's doings, more by the sum of results obtained, than by appearances, which are proverbially deceptive.

Experimenting, however, is on an entirely different plane from that of regular production, and calls for a few remarks. It is axiomatic that experimenting should, as far as possible, be kept out of the works, because experience proves that it may be very costly to mingle experiment with systematic production. The importance of this vital business principle can scarcely be overstated. Although it is academically understood by most directors of practical affairs, its full significance is seldom clearly realized. Most people regard, certainly with no disfavor, the idea of progressive improvement, which is naturally associated with general intelligence. But I very much doubt if many draw a sufficiently sharp distinction between works practice and experiment; and in consequence I suspect that much of industrial progress and improvement is unnecessarily costly, and destructive of best practical efficiency. I do not doubt even that a large

number of the improvements made in works methods by too progressive managers, never pay for themselves at all, if the accounts could be properly examined and subdivided in a truly informing manner; whilst as regards others, though they may pay well in time, yet their introduction disturbs the course of systematic production quite seriously. The best kind of manager for practical works, other things being equal, will be the one who refuses, stubbornly, to mix his experimenting with his systematic production. The latter, in fact, should only be undertaken on clearly defined lines. Every pound of material and every hour of time expended should, in regular production, be made to yield once and for all its desired and calculated result. The improvements from week to week should be those of organization and systematizing. A first-class executive manager to-day will bring such things as operating costs and percentages of recoveries, renewals, etc., down to a great degree of refinement, studying his monthly (or even weekly) cost sheets, with the continuous fixed attention with which a driver regards the road in front of him; whilst every employer of labor knows how much more effective and easier to himself a laborer's or a mechanic's work will become by systematic repetition of his task. It is just the same with the cost of systematic production in a works.

From every point of view, either of employer or employed, improved industrial results are eminently desirable. For no one who thinks intelligently at all on the great questions which influence industry in our day can any longer imagine that any permanent betterment of the employed classes can arise through methods which are calculated to injure the industry itself, or to cause waste and extravagance, as a whole, in the processes of production. The process of all production in fact must be looked upon as if it were (as it actually is) for the common benefit of humanity, however unfair or unrighteous may be the process of distribution of the results. Those who would be efficient political or social reformers must address themselves to the latter problem mainly, and see that they do it in such a way as not to injure the true economy and efficiency of the world's industrial production which has already attained to a high degree of perfection. Otherwise all such supposed reform will be merely retrogression.

II.

In spite of the desirability of the rigid exclusion of experiment from the actual scene of systematic production, there is to-day a growing belief that experiment must nevertheless not be too much neglected. When one studies the curious history of most inventions, the early struggles of many inventors (like Bessemer, for instance) to get even a chance to demonstrate the suggestiveness of their ideas, let alone to laboriously and expensively work them out to finished issues; and when one looks back only a few short years, and realizes the immense wealth which has been so rapidly created by the application of these ideas as soon as they found intelligent application, also the great lapses of time which usually take place in real life before such applications are realized, the conclusion is forced upon us that we are still very far short of the high-water mark of intelligent organization in this, as in other mundane matters.

I am personally of the opinion that before the problem of quickly and readily determining the wise limit of experimenting will be solved in an efficient manner, some far-reaching and radical changes in our system of encouraging and protecting progress and invention must be brought about. The root of the difficulty I believe lies in the fact that the whole mental principles necessary for the promotion of improvements in industry are radically opposed to those necessary for sustained cheapest systematic production.

The preponderately influential element in manufacturing progress is the financial element. It is scarcely too much to say that it is the only really powerful element; but there is a great lack of coördination between this and the technical element (or the scientific workers, constituting the best intelligence of the world). A brilliant but unsuccessful inventor once bitterly declared in my presence that to be a successful "business man" it is necessary to be "intensely stupid"; and there is a germ of truth in this epigram, if we mean by stupidity the inability to see anything except what is right in front of the nose. The intellectual qualities and personal temperaments of the leaders in business enterprise and in scientific pursuits will in most cases be entirely different, and it is only the most

highly gifted of each of the two classes who will understand and appreciate each other properly.

The average inventor, looking only to the future, and to the development of his broad ideas, will usually overlook the importance of the present moment, and, if placed in charge of active operations will often attempt to reorganize important matters of routine far too frequently. The temperament of the inventor, too, is allied to that of the artistic genius and other abnormal varieties of the human species, and he is inclined to be erratic, unreliable, and even incompetent in daily routine work. A common failing of his is lack of persistence in any one direction. Long before one idea is worked out his mind is off on to another, and the first has lost interest for him. Even when he is capable of a sufficient degree of concentration on one object, he is apt to overlook the importance of that steady piling up of small items of cost, and small lapses of time, which so often mean big bills of cost and low outputs at the end of half a year. So much is this the case, in fact, that it is no uncommon thing for an invention to fail entirely of commercial success in the hands of its author, and subsequently to reach great success in other and perhaps less gifted hands. The business man and the ordinary routine technical man, on the other hand, alike, usually absolutely lack that divine spark, which is necessary for every kind of advance in human affairs, and so are powerless to effect anything but the most trivial changes in any operation which is placed under their direction. All that is in the least degree outside what has been learned by such men in the study of their profession, appears alike dangerous and unworthy of consideration. The mind of such a man moves in a beautifully defined and regular orbit, but he is often absurdly timid and incompetent in anything which he has not done or seen done before. He is apt also to regard the professional practice of his day as if it were the final summit of human attainment, and altogether to despise and undervalue those who would attempt to go beyond it, and he will gloat over the failure of an experiment as if it were a foregone conclusion and merely serves to confirm his narrow view of possibilities. One involuntarily compares his mind with that of primitive man, to whom the darkness of the forest or of the night are alike synonymous with all mystery. In consequence of this attitude of mind, he has small powers of discrimination in matters

of invention, and all inventors to him are divided into two classes: they are geniuses if successful, and madmen if they fail.

Most of the great leaders of finance, of course, are exceptions to the kind of qualities I have indicated as appertaining to the "routine man." They will approach nearer to the inventor in temperament than to the ordinary business or routine technical man. They are, in fact, sometimes a happy blending of the two temperaments, and therein lies much of the secret of their success and power.

There is no high court to which an inventor to-day can confidently go for justice and help with his ideas; and there is no one in the whole world to say who amongst the many people with ideas is the genius and who the visionary madman, until after a trial, to effect which it is necessary in the meantime to expend capital. Such discrimination is inherently very difficult.

In this dilemma, when confronted with any new idea now, the man of affairs (and purse strings) must usually turn to his "routine technical man" for advice, or else use his own admittedly defective judgment. The advice he gets is naturally often not sound, because it has usually no premises to start upon. In consequence, many mistakes are made, and every director of affairs knows this well. But, as in all practical affairs, the difficult question to answer is, "How can it be otherwise?" It is impossible for any but the very largest and wealthiest concerns or individuals to keep their own Edisons, with a complete outfit, on their own premises; and even if it were possible, it is not one Edison but a hundred they would require to keep up to date in all the branches which a modern industrial business touches upon.

In the net result to-day, the inventor who takes his invention where common sense would dictate, viz., to the large producer of the specialty concerned, is usually politely shown the door, with many pleasant expressions of regret and excuses (which he knows are not truly apposite), no matter what he has to offer, and he is then driven to ponderous efforts to imitate works conditions in his own back yard. His support during the "back-yard period" (unless he is of the minority who are rich) usually comes from over-sanguine speculators, who perhaps have made an early lucky hit and are now steadily working down their average in vain endeavors to hit the mark of speculative success again; or from personal friends, whose

faith in the general character and ability of the inventor makes them willing to risk money on his chances of success without aspiring to any knowledge of his specialty. The latter, it is perhaps needless to say, in course of the lifetime of such an unfortunate, often become fewer, and the length of his active career is apt to depend less upon his actual inventive ability than upon sheer luck, and his accidental associations, social relations, personal powers of persuasion, or "personal magnetism." Many good inventions are killed in this painful and illogical process; and the histories of nearly all great inventions of the past decade or two show quite markedly something of its delaying, retarding, and demoralizing influence in the noteworthy circumstance that scarcely ever has a great patent commenced to earn any money for its owners until it has been within a few years of its expiry.

In spite of this, when a patent pays at all it usually pays so well that it is quite a rare thing for the term of any patent to be extended, although a special provision is made by law for the very contingency we are discussing. The early years of most patents are consumed in financial struggles and difficulties. If one is at all promising, it usually becomes a subject for speculative dealing at a very early stage. The inventor gets a very small sum for his encouragement to further indiscretions, and the monopoly passes into the practical control of the capital interest, which may either work it for all it is worth, as soon as its success is demonstrated, or may just as likely hold it inactive to prevent competition. And so the world is still dependent for its progress in this matter, as in so many others, upon the natural selection of chance and opportunity.

This means, in short, that that great guiding principle, the human intelligence, which has wrought such wonders in the analytic examination of man's environment, has not yet, in its constructive efforts, reached into this department of man's business or industrial activities. In such matters we are still almost in the savage state of nature. We hunt around, and root about, for ideas, and when found, we scramble for the fruits of them in the time-honored fashion which descends to us from our simian ancestry.

III.

I shall here, very briefly, attempt to outline a scheme which suggests itself to me as a practical means to meet the needs of the case we have been considering as they are to-day. I cannot hope that it can be anything more than a mere suggestion, of more or less doubtful value; for I cannot claim to possess either the natural endowment or the opportunity to bring such an idea any further than the stage of suggestion. For what it may be worth I therefore give it as a suggestion.

The present patent system is admittedly inadequate and bad, although the department of patents in many countries is well organized and admirable in many respects. In fact, the whole current of ideas about protecting the inventor seems to be based on antiquated principles, and an imperfect understanding of the problems involved.[1] The question, then, is how best to bring it up to date. I think that in order to do this we must look at the subject from a much more comprehensive viewpoint than that usually selected as the starting point of reform. In the first place, important as an "idea" admittedly is as a factor in the progress of improvement, yet it is by no means the only factor. There are many steps between the inception of an ultimately useful "idea" and its commercial application. Yet in all our protection laws, no account is taken of such steps, beyond the crude endeavor (which the principles of these laws indicate) to insure that the patented idea shall be technically workable, and to give the actual inventor a certain amount of time to bring his ideas to perfection before other people are allowed to compete in the use of the resulting process or apparatus.

It often happens that the inventor has no means at his disposal to do this. Often, if he had ever so much means, he is not capable of doing it. Often, he loses heart and interest in the particular question long before the patient, sustained effort necessary for any final accomplishment is performed; and he seldom in actual practice realizes for himself, or for his idea either

[1] The very term of the patent (fourteen years in most countries) is based on the old-fashioned term of seven years for an English apprenticeship, and was supposed to afford the inventor the opportunity of teaching the patented "art" to his second apprentice before it became public property. Needless to say there is not a trace of present-day applicability in the original idea of this association.

the kind of protection or the utility intended by the law. Yet to him is given the monopoly, if he can only sit down and write out a reasonable specification, embodying a novel idea and one (more or less practical) method of working it. It need not even be a profitable method commercially.

On the other hand, occasionally, large sums are obtained by somebody (not often by the inventor) through the protection given to some simple idea, for which a valid patent is obtained at a suitable time, and proves capable of surviving all attacks, and weathering the vicissitudes of a legal campaign. In this process a patent becomes of established value, perhaps at a time when other commercial conditions of the industry are propitious. From such cases, promising patents have come to be invested with a kind of speculative value, very foreign to the root ideas underlying the original grant of such privileges. I need not enlarge upon the inadequacy of the actual "protection" which falls to the lot of the inventor under this system. It often amounts to very little; but there is no protection at all (except his own possible lack of enterprise already noted) for the purse of the capitalist against the depredations of predatory inventors, under the influence of whose alluring blandishments he may innocently fall; and there is no protection at all except a rigid secrecy (which has consequently become the general rule in all novel and intelligently planned industrial undertakings, and is of immense detriment to the industry as a whole) for that very large and important kind of right, represented by the expenditure of time, money, and talent in working out and bringing details of works or processes to commercial perfection.

Manifestly it is no easy matter to legislate adequately to meet all the various and rapidly changing conditions of modern industries, and complicated legislation is proverbially dangerous. My proposal to meet this case, however, would appear to be fairly simple. It involves: *First.* The enforced publicity of all details of industrial practice. *Second.* The abolition of the present patent. *Third.* The creation and distribution of a fund to be distributed yearly or half yearly by means of a tax on production calculated every year as a fixed percentage of the increment due to improved methods, and the periodical distribution of this fund by a competent board of trustees to experimenters, inventors, or would-be improvers

in any industrial operations who have either registered their ideas or their line of work in advance, and obtained the necessary sanction for state expenditure, or have at their own cost worked at something and can now substantiate claims to be the originators of useful improvements in the arts. *Fourth.* The conversion of the Government patent departments into a court of arbitration, registration and inspection, whose main office would be the distribution and division of the yearly subsidies collected under (3), and the assessment of the taxation to various producers.

No doubt many difficulties would arise under headings three and four, but they do not appear to me to be of any greater magnitude than the many difficulties already successfully dealt with by taxation departments and other departments of a modern civilized government. Even if some injustice were done to individuals in the extent of recognition or taxation awarded or assessed (and it would be sanguine, indeed, to hope to entirely escape such injustice), it could scarcely by any possibility be so great as the many injustices and inadequacies inherent to the present system. The abolition, on the other hand, of the extremely speculative element, inherent in long-term patents of unproved value, and the absurdly inadequate and difficult system of assessment of merit now attached thereto; the important step of enforced publicity and public property in all improvements (making for much more rapid progress and keener competition in all industrial practice) and finally the graduated scale of reward for all useful works or genuine effort, whether by capitalist or inventor, could not but result favorably for the industry as a whole. The encouragement of invention, and of commercial development under such a system, would be adequate and steady, and the actual sums distributed to inventors, or expended on experimental research, would bear some reasonable relation to the utility of their productions. The expenditure (being a percentage of the profits from the industry) would also bear a reasonable relation to the fluctuating market values of the products and costs of production. At the same time individual unaided enterprise would be absolutely free to compete for the prizes as it does now, so that true commercial ability would stand on its own bottom.

Until some such radical change is brought about (and the

principle of vested rights, involved in existing patents, will demand that it must come slowly) manufacturers cannot do better than to have their own experimental staff, and laboratories, and to keep them as far as possible quite independent of the works, whilst giving them all the advantages of frequent observations at the factories. I also believe that in spite of the apparent injustice to oneself involved in publishing, unrewarded, details of one's own improvements, manufacturers will more often gain, in point of fact, than lose by adopting the more large-minded and generous attitude, and I hold that view, not from merely unsupported sentiment, but because I have observed very often that the open attitude promotes an attitude of inquiry and exchange of ideas which is extremely healthy to any industry. Out of ten men whom one rubs against in a year, five may have some kind of idea or suggestion to impart, but only one will be a probable competitor in your business. The gain from the five will, I believe, in most cases, be greater than the loss from the one. Of course there are exceptions, but I believe they are far fewer than is supposed, and a more open policy all round would be a truly wise one, as it has already proved in the larger sphere of world politics.

IV.

But such matters, however interesting, lead us beyond the legitimate scope of this book, and we must now return to our subject. The cost of production, capital charges, value of products, and percentage of recoveries being accurately known, I have shown that it is a matter of common arithmetic (or book-keeping) to make any computations of results or of capital needed, to produce such result; always excepting the case in which any change occurs in the value of the products between the time of an estimate and its putting into practice. Such changes occur quite frequently, and a comparatively small change in metal values may convert a good profit into a heavy loss for in some cases we are dealing with high values, and also the cost of production in many cases remains the same, or nearly the same, whatever the value of the product.

In order to fully illustrate this all-important subject of fluctuating metal values, and at the same time to afford useful information for reference, I have prepared the following series

of fifteen diagrams of all the leading industrial metals giving (1) price, and (2) production, during the past half century.

Similar diagrams relating to the principal derived electrolytic and electro-thermal products, heavy chemicals, etc., but for a

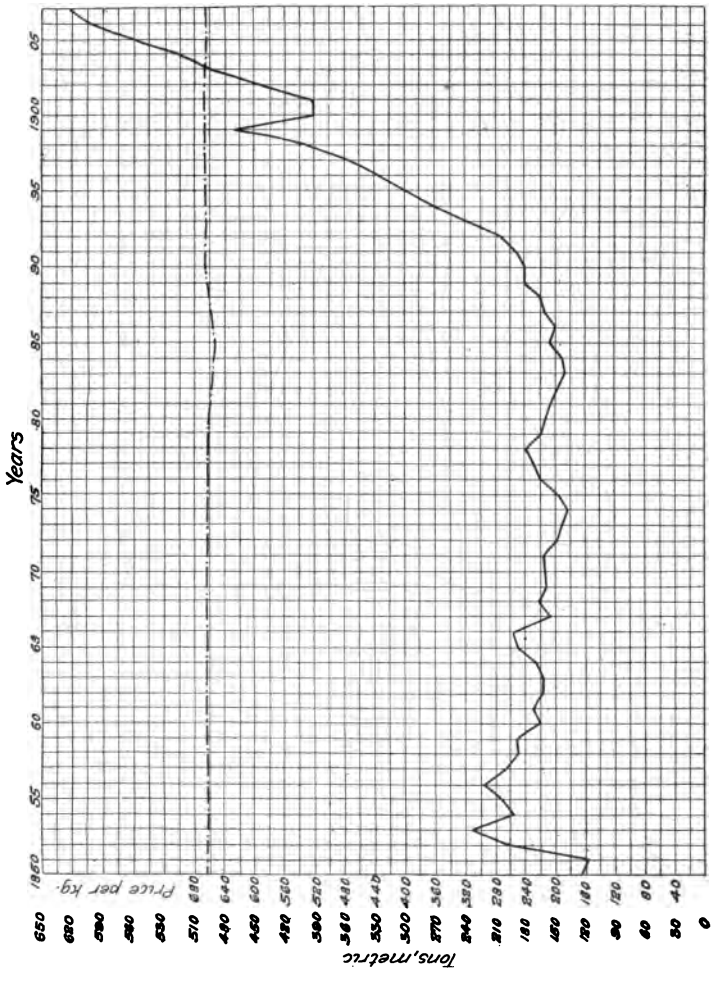


Fig. 3. Gold: Production (solid line) and Price (dot-dash line).

shorter period only, will be included in the respective chapters dealing with each product in the sections of the book which are to follow.

Very complete statistics are obtainable for *gold* (Fig. 3) and

the output, as will be noticed, has been pretty steadily increasing almost without interruption during the period reviewed. As the price of gold is a standard for all other values, the fluctuations (unlike those of any other metal) are only trifling,

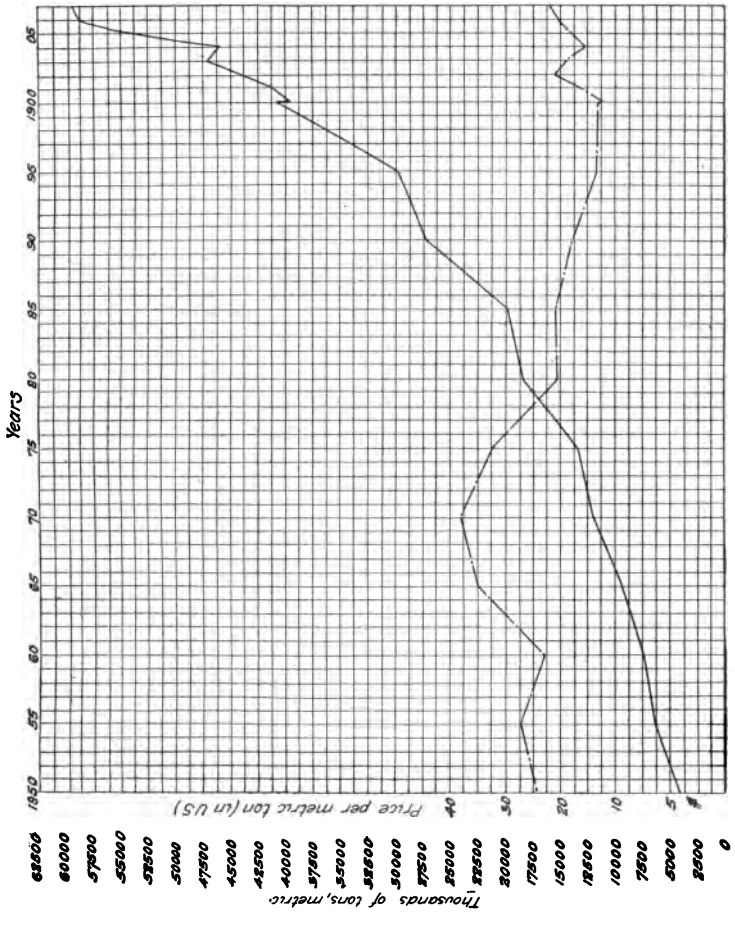


Fig. 4. Iron: Production (solid line) and Price (dot-dash line).

and relate to such matters as the distribution of the relative demand for and supply of ready money to conduct the world's banking transactions in various localities. The production is given in metric tons, and the price in dollars per kilogram. The time is in five-year periods.

Its production is only in small part electrolytic.

Very complete statistics are also obtainable for *iron* (Fig. 4). The production has shown a phenomenal increase of late years, and appears to be steadily accelerating. The price, like that of



Fig. 5. Nickel: Production (solid line) and Price (dot-dash line).

almost all other metals, has responded to waves of prosperity and depression with a fair degree of uniformity throughout.

Its production at present is scarcely influenced by electrolytic or electro-thermal processes, but a change in this respect may be impending, owing to recent developments.

Allied to iron chemically, *nickel* (Fig. 5) is so much rarer that only of late years has it come into any extensive use. As a consequence both prices and production have fluctuated violently,

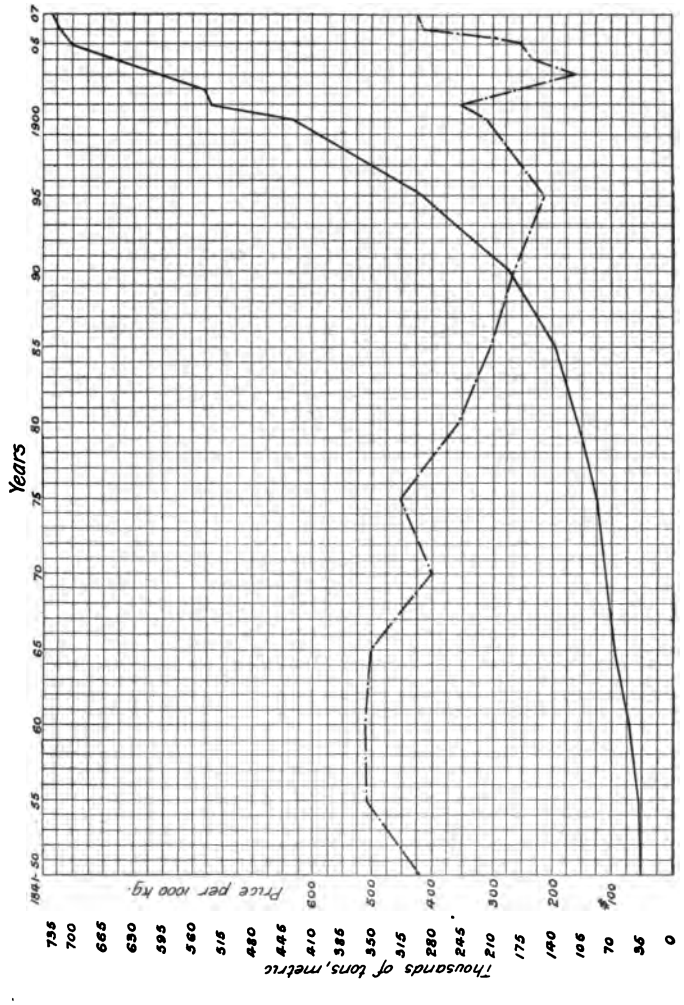


Fig. 6. Copper: Production (solid line) and Price (dot-dash line).

following the very general trend of all the metals. However, the sum of all the progress is a great extension of the production and a steady fall in the price.

The metal has some importance in relation to electrolysis,

because it is extensively used for electroplating on iron, although it is at present won exclusively by ordinary thermal methods.

Copper (Fig. 6) is also a metal of which ample statistical material is available. It has had an enormously increased output in

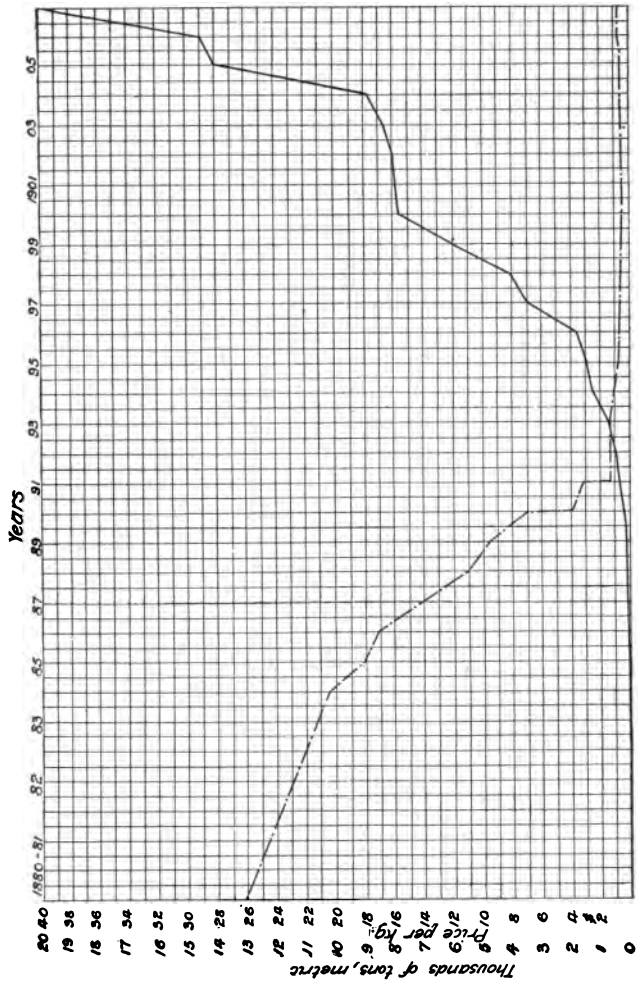


Fig. 7. Aluminium: Production (solid line) and Price (dot-dash line).

recent years, the greater consumption being mainly owing to the development of electrical engineering. The price has been well sustained, but fluctuates like the other metal values and largely in unison with them.

A large proportion of the output is now refined by electrolytic methods.

Aluminium (Fig. 7) is the product solely of the last fifteen years, and the bulk of the demand has only arisen during the

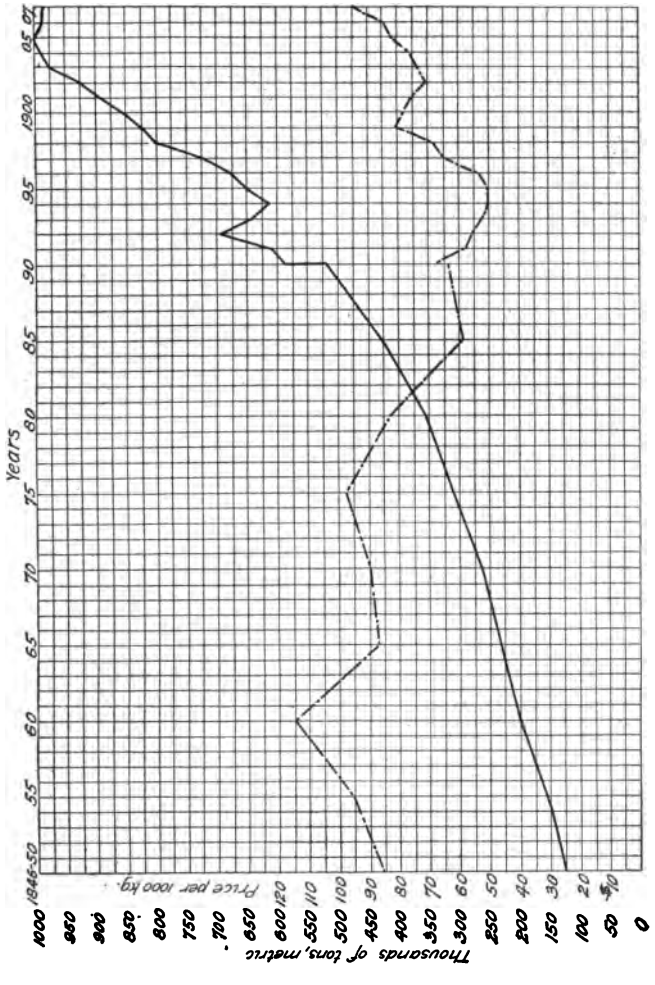


Fig. 8. Lead: Production (solid line) and Price (dot-dash line).

last five years. It seems destined to play a very prominent part in the metallurgy of the future.

It is produced exclusively by electrolytic methods.

Lead (Fig. 8) is an old established metal; following almost exactly the progress of copper developments the curves of this metal show the same characteristics of steadily increasing output, and irregular but roughly periodical rises and falls in value, with some permanent decrease for the whole period.

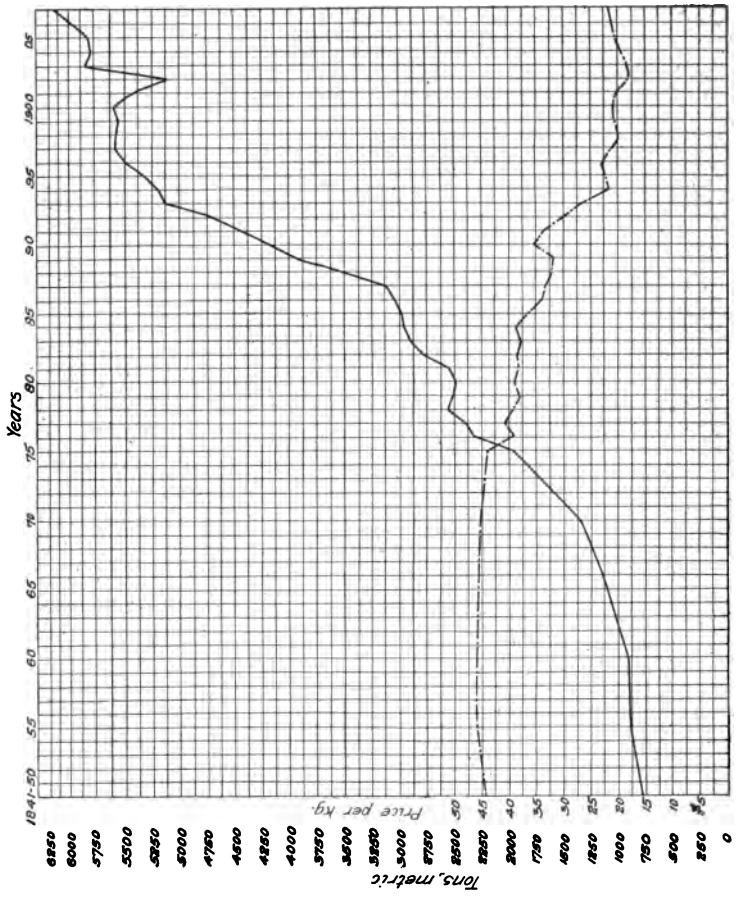


Fig. 9. Silver: Production (solid line) and Price (dot-dash line).

Very little lead as yet is recovered (or even refined) by electrolytic methods, but there are substantial indications of coming changes in this respect.

Silver (Fig. 9) is also an old established metal and follows very closely the progress of lead, for much silver is mined in association

with lead. The production has shown a steady and remarkable increase for the whole period, with a recent slight falling off. The price well sustained (largely by artifical means) until 1875, declined irregularly from that date until 1890, when it broke

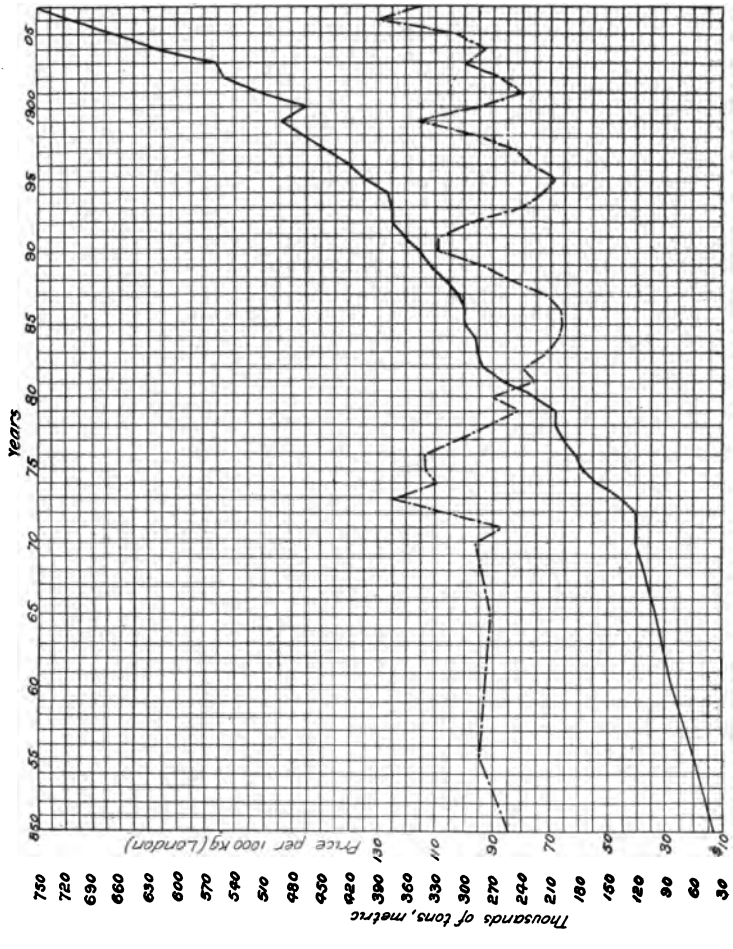


Fig. 10. Zinc: Production (solid line) and Price (dot-dash line).

completely and has never recovered much more than half its original value.

A good deal of silver is refined electrolytically.

Zinc (Fig. 10) is also an old established metal, but of more recent history than lead or copper. A steady increase in

production with rapid acceleration in recent years characterizes the curve, and the price displays a very remarkable instance of the regular periodic fluctuations to which all metals tend.

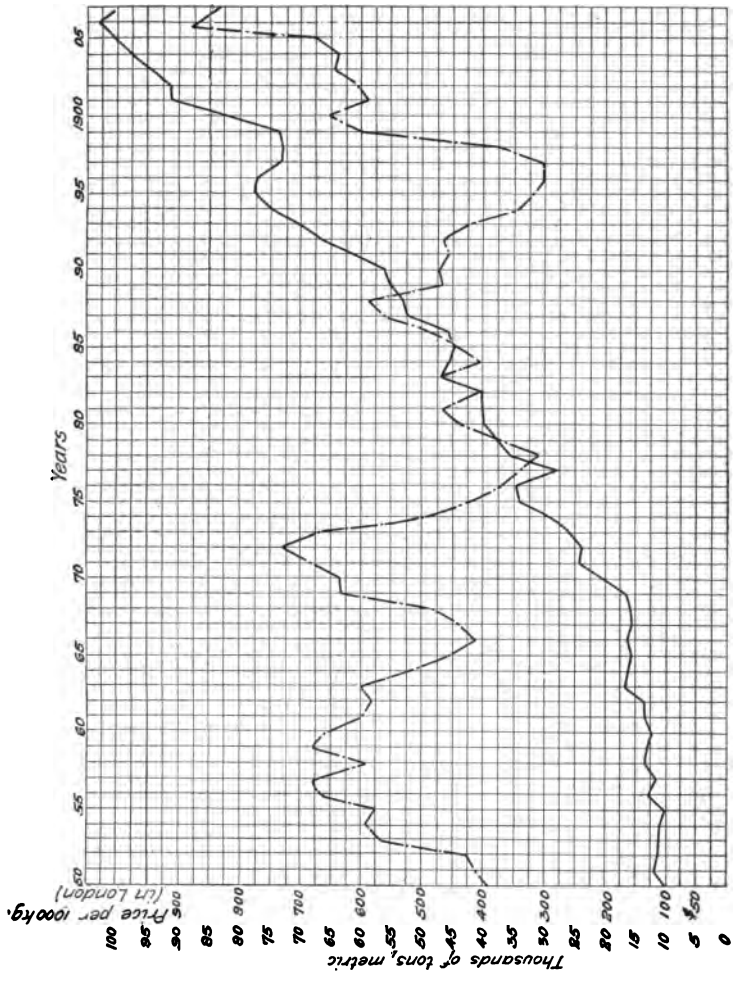


Fig. 11. Tin: Production (solid line) and Price (dot-dash line).

Very little zinc is as yet recovered by electrical means, but changes in this respect due to recent experimental developments are also possible. Almost the same remarks apply to *tin* (Fig. 11), but, whilst the production has been steadily increasing

over the whole period, the periodic fluctuations in price have been greater perhaps than for any other metal.

Small in itself the production and price of *cadmium* (Fig. 12)

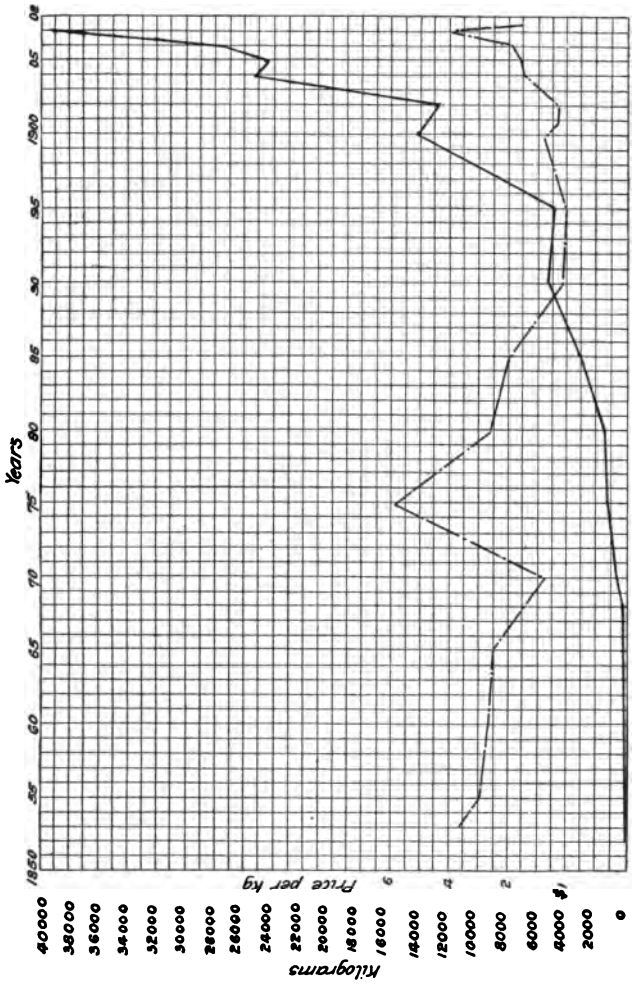


Fig. 12. Cadmium: Production (solid line) and Price (dot-dash line).

have closely followed those of zinc, with which it is always associated.

Antimony (Fig. 13) has followed the general characteristics of the other metals, but shows some falling off in production in very recent years, and a recent remarkable fluctuation in price.

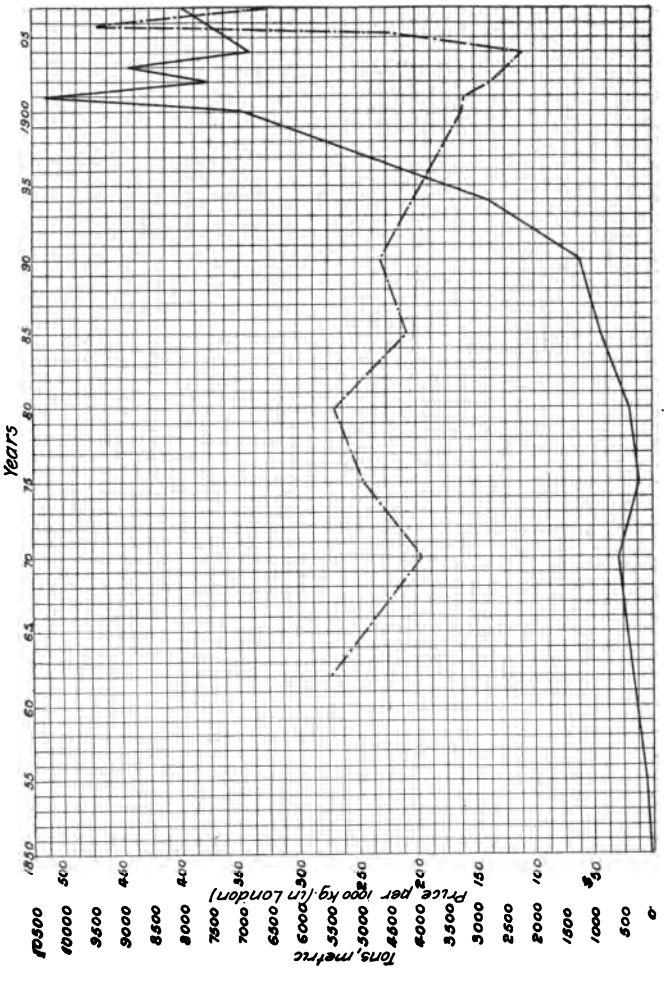


Fig. 13. Antimony: Production (solid line) and Price (dot-dash line).

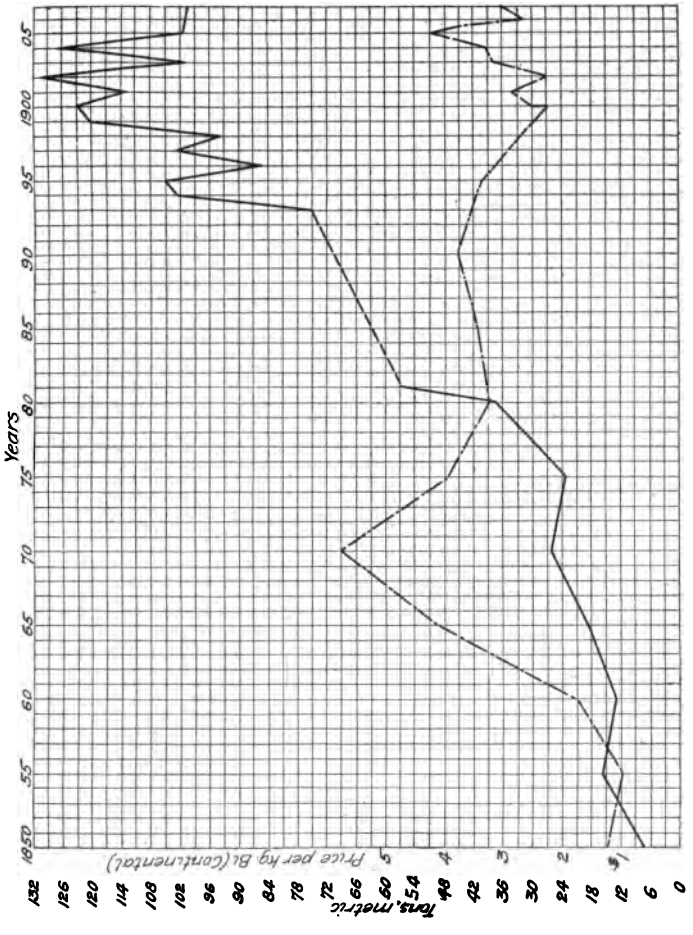


Fig. 14. Bismuth: Production (solid line) and Price (dot-dash line).

Bismuth (Fig. 14) has a somewhat irregular history, with a tendency, however, to the same general characteristics as the others.

Mercury (Fig. 15) is a more specialized metal than any of the former, and the curves display more undecided characteristics.

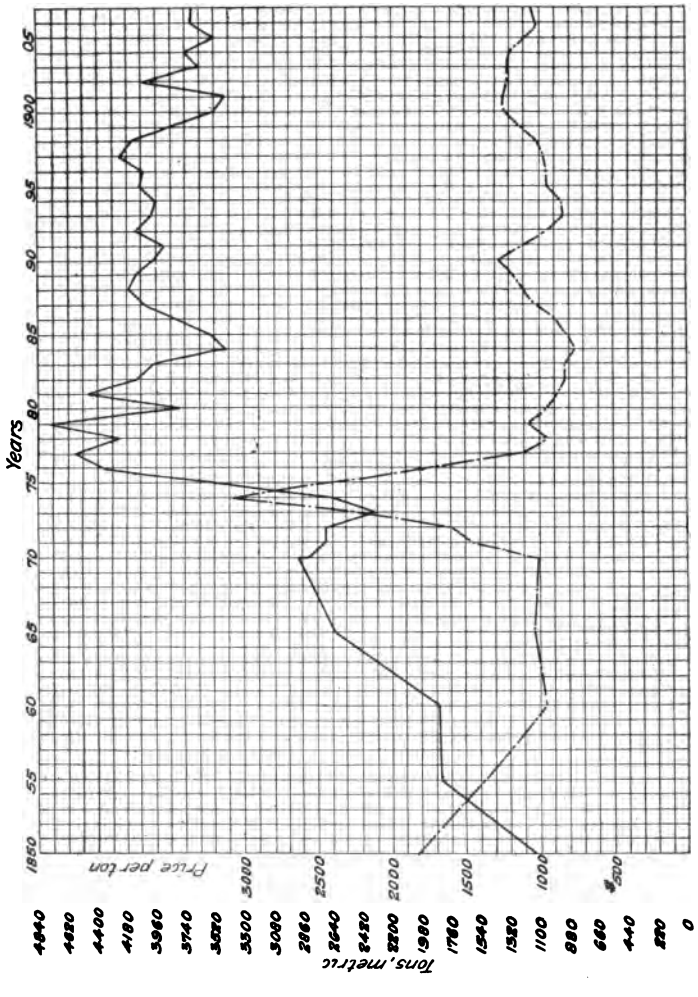


Fig. 15. Mercury: Production (solid line) and Price (dot-dash line).

There is still, however, the same general tendency to steady increase of demand and periodic fluctuation, with an average decline in price.

Sodium (Fig. 16) has properly no history, speaking in a commercial sense. The great bulk of the production has been during the last eight years, and the price has been well maintained, while the recent ratio of increase of production has been greater than for any other metal except aluminium.

The metal is produced exclusively by electrolytic methods.

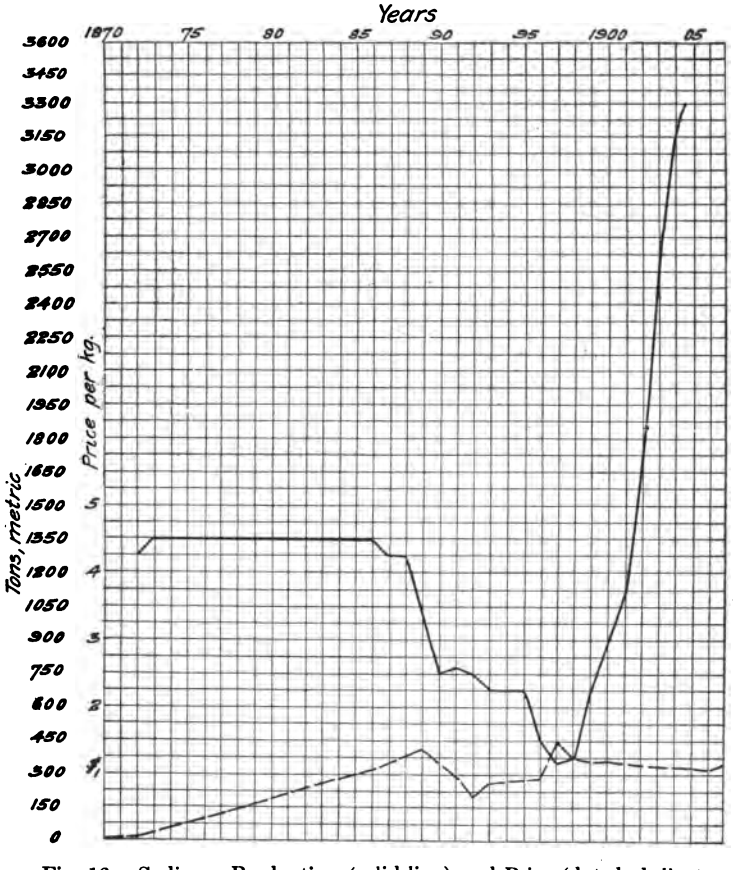


Fig. 16. Sodium: Production (solid line) and Price (dot-dash line).

The great scarcity of *platinum* (Fig. 17) in nature, coupled with its great utility in the arts, has produced occasional periods of excessive demand leading to very high prices and a steady augmentation of average price. It is curious to note that 25 per cent

of all the platinum which goes into use is said to be stolen and no return for it given to the mines or smelters by the workmen.

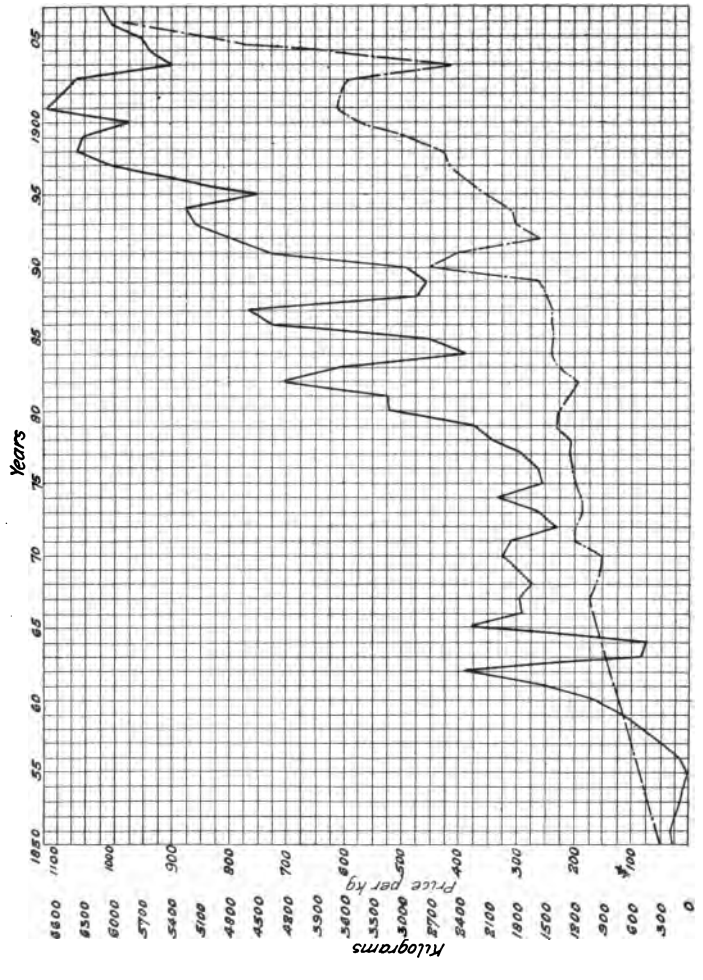


Fig. 17. Platinum: Production (solid line) and Price (dot-dash line).

It should be borne in mind in studying these tables that, for all purposes of broader consideration, demand and production are identical, for the world's stocks of any metal are never very large.

V.

The two most striking features revealed by a study of these histories are practically alike for all, viz., (1) The great increase of the demand for metals of every kind which recent years have brought about, and (2) The peculiar periodic rise and fall of prices, coupled with a general average decline in values, displayed by all metals whose ores are abundant in the world; and conversely, a rise in average values, coupled with similar periodic fluctuations of price, for all metals whose ores are scarce in nature. Rare metals, like platinum, have not shown so great an increase in production as others. There is a tendency in such cases to find substitutes. Gold, however, for evident reasons is an exception to both these rules.

Wherever a demand for any industrial product arises capable of being met by improved methods of production, such improvements are sure to overtake, and even outstrip, the growing demand. When, however, the natural source of the metal or product is scarce, then the reverse process takes place, and results in an increase of market values due to increased cost of raw material which tends to restrict the further use of the metal or product.

A few exceptions to this tendency, like the standard metal, gold, — and like the commercially new metals, sodium and aluminium — two metals which have maintained a high price with increased production[1] — do not disprove this rule. Gold is unique amongst the metals because of the now almost universal gold standard of currency. The other two metals are produced solely by electrolysis, and by a single, patented process in each case. In consequence, artificial conditions have been brought about, and there has been no time to find a true natural level as yet. There can be little doubt that when these artificial conditions are removed with lapse of time, the prices of these two metals, whose ores are so extremely abundant in nature, will show some decline, and possibly a very large one.

Besides the above metals, for the winning of every one of which electrolytic and electro-thermal methods have been either already extensively applied, or have been suggested, there are a

[1] Both these metals have, however, experienced heavy falls since above was written.

few leading heavy chemicals and special industrial products which have been the cause of considerable commercial activity during the last twenty years. These are:

1. Caustic alkali and bleach.
2. Products derived from electrolytic chlorine.
3. Carbide of calcium.
4. Nitrate of calcium.
5. Hypochlorite solutions.
6. Ozone.
7. Oxygen and hydrogen gases.
8. Artificial graphite.
9. Artificial emery (carborundum, aluminium, etc.).
10. Sodium cyanide.
11. Sodium peroxide.
12. Potassium and sodium chlorate.
13. Phosphorous.
14. Ferro and aluminium alloys and other reducing agents for iron impurities.

Every one of these industries is in progress to-day at Niagara Falls and at other power sites. But it must not be supposed that all these manufactures are by any means readily available to the public. In some instances the best processes are of so recent production that they still are protected by patents; and in other cases, although the actual patents on which the processes were started have expired, the industry has been kept closely secret by its founders, so that intimate knowledge of its practice is not to be obtained outside the circle of those already practicing it. Few electro-chemical industries have as yet passed beyond the latter stage, and this is more particularly true of a few of the more highly profitable ones.

But it is reasonable to suppose that the coming decade will change these conditions considerably, for it is not possible, for long, to keep commercial secrets for unprotected industries, on a large scale. Just at this juncture nearly all the older, leading patents have expired or are about to expire. This factor alone cannot fail to work in the direction of freer competition amongst successful industries, leading to greater expansion of the scope of activities of the two divisions of modern industry which are discussed in this book.

CHAPTER V.

GENERAL DESIGNS FOR INDUSTRIAL PLANTS.

I.

CERTAIN necessities arise with a recurring frequency in the practice of the arts we are considering, and the following description of generally prevailing technical conditions, and of various special devices, will be useful.

Electro-thermal processes. Where the effect of the electric current is to be merely a heating (or Joule) effect, it will generally be found more economical, as well as more convenient, to employ alternating-current generating machinery. The cost of this is, usually, considerably lower per kilowatt of capacity than that of continuous current machinery; the cost of upkeep is less, mainly because the collecting arrangements are simpler; and finally a great advantage exists in the facility with which such currents can be carried over considerable distances, converted from high to low voltage or current, or vice versa, in any desired quantities, by means of stationary transformers, without moving parts. For these reasons alternating currents are used wherever possible. They will be almost exclusively employed in such industries as carbide, carborundum, or graphite manufacture; iron smelting, nitrogen fixation, or zinc distillation—not in zinc electrolysis.

I cannot of course enter at length into the design of the generating plant, as that is a special subject by itself. We must imagine that a high-tension current is received from some public (or private) source of supply, which is quite independent from the manufacturing department.

The first consideration in designing a plant is, then, the transformer, which must be equal to any variation of load likely to occur in practice. The details of such apparatus, and of their controlling mechanism are now also matters of general elec-

trical engineering knowledge and specialized practice. Therefore only the furnaces, and like apparatus, and a few supplementary devices will be here described and illustrated for the purpose of showing how electric currents are utilized in practice on a large scale.

The two leading types of furnace are the "arc" furnace — a device which provides a high temperature in a very circumscribed space, — and the "resistance" furnace — an arrangement

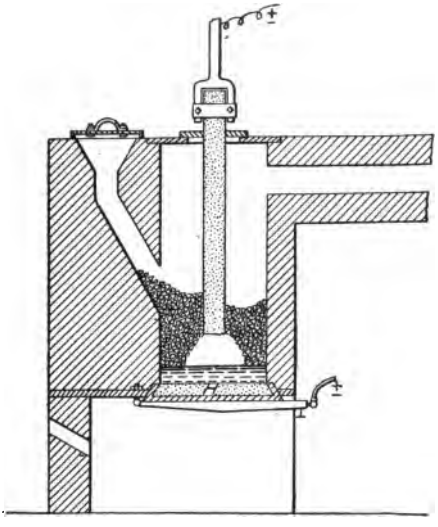


Fig. 18. Arc Furnace.

which may also be made to supply fairly high temperatures, but with the heat much more widely distributed.

The following five cuts are typical forms of apparatus for operating with alternating currents.

The *arc furnace* (Fig. 18) utilizes the "arc" between a stationary lower electrode — formed of the movable hearth and the molten charge — and a movable upper electrode — formed of a carbon slab or rod. The mixture is led through an oblique side aperture, and any smoke or vapor which is formed escapes through a side flue. The charge is periodically withdrawn by opening the swinging hearth door. Such furnaces are sometimes used for producing carbide of calcium, also for ferro-alloys and iron smelting.

Any value of current, from 1,000 to 10,000 amperes, can be made to operate such a furnace, if the parts are suitably designed; and the electromotive force required to strike a good "arc" will be from 30 to 60 volts according to the size of the apparatus and the nature of the charge.

The *resistance furnace* (Fig. 19) utilizes an entirely different principle, — that of the resistor. A core of conducting material is very carefully packed between two mounted carbon electrodes

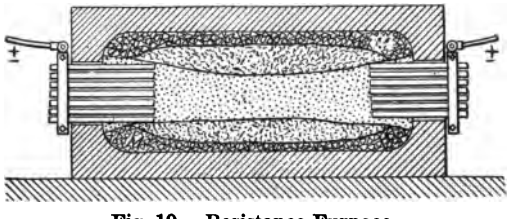


Fig. 19. Resistance Furnace.

fixed at a considerable distance apart (from ten to fifty feet in large furnaces). This core is surrounded by a layer of the materials to be acted upon by the heat, and the whole is surrounded by more material and layers of heat-insulating materials; and finally by an outer case of loosely placed bricks. The

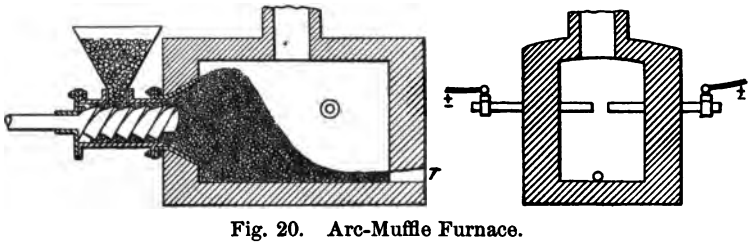


Fig. 20. Arc-Muffle Furnace.

charge is then "fired" for a suitable time, by passing the current, after which it is allowed to cool, and the product which forms round the core is picked out, broken up, sorted, and packed. In some operations of this kind more than one product is formed by reason of the different zones of temperature. Such furnaces are used for making artificial emery and graphite.

The *arc-muffle furnace* (Fig. 20) is a modified type combining the principles of an "arc" furnace with the effects of a "resistance" furnace, by enclosing the charge in a muffle and exposing

it to the radiations from the arc and from the sides of the muffle. The problem here is to distil and reduce zinc ore, as in the ordinary zinc muffle; but it is necessary to avoid the bad effects of "fusion" of the charge before the reactions are complete. The charge is fed in uniformly, and the slag tapped off in a thin stream, whilst the product sought distils over.

The *arc furnace* with pre-heating or regenerative attachment (Fig. 21) (iron) is a novel type of arc furnace designed by Héroult (not yet operated). The object of the furnace is the economical

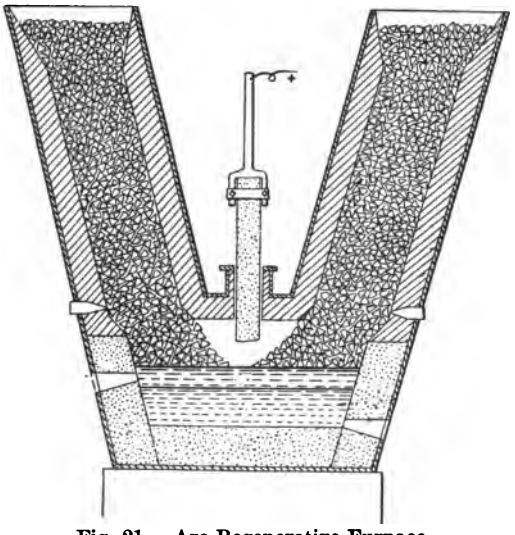


Fig. 21. Arc Regenerative Furnace.

smelting of iron ore in admixture with a small percentage of carbon. The two side hoppers are treated to a blast of air, whereby CO gas is oxidized to CO_2 and the descending charge is heated up considerably. In this way much energy is saved. The particular construction shown obviates the danger of the rapid consumption of the carbon electrode by the air blast. The movable electrode must pass through a gas-tight gland and stuffing box. Slag and molten iron are tapped from the hearth by two tap holes, placed at different levels; and the whole is suitably lined, with the object of confining the maximum possible quantity of heat.

An altogether novel and distinct type of furnace of which

many examples have been designed and patented during the last few years is the type known as the induction furnace (Fig. 22), wherein the charge, being a conductor of electricity, is heated by a current produced in it by a surrounding or adjacent magnetic apparatus. The illustration shows diagrammatically Mr. Albert

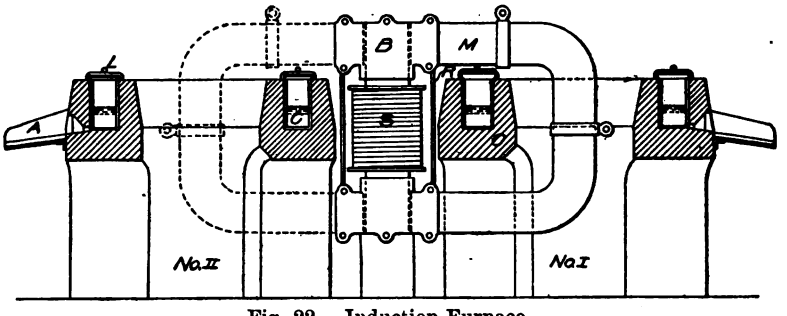


Fig. 22. Induction Furnace.

Hjorth's continuous electric induction smelting furnace, which is a recent form of Kjellin's and former inventors' idea.

It may be compared with an ordinary transformer.

The alternating current is led to the spool, *S*, consisting of insulated copper wire wound round the fixed part of the magnet, *M*, whereby a low-pressure current of high intensity is produced in the circular furnace, *O*, which surrounds one of the limbs of the magnet, and contains the charge, *C*. The charge in this case corresponds to the secondary winding on a transformer, and it follows that for the successful operation of such a furnace the charge must be a conductor of known and stable resistance.

When, for instance, a current of 900 amperes at 300 volts is led to the spool, a smelting current of approximately 30,000 amperes at 7 volts is obtained in the charge (the efficiency being $\frac{7}{8}$).

By this means the smelting current is transmitted to the material in the furnace, *C*, without the use of electrodes.

Many forms of this "induction" idea have been recently suggested, but as far as I am aware, few have been tried on more than a purely experimental scale. A modified form of the above furnace (by the same Norwegian inventor) has the secondary, or smelting circuit, broken by the interposition of a pair of carbon electrodes, whereby the two forms of "arc" and "resistor" heating may be combined.

The *magnetic thready arc furnace* (Fig. 23) (nitrogen) is again an entirely different and novel type of furnace employing long, thready arcs, produced by a high tension and feeble currents between cooled metal electrodes. The arcs are caused to continu-

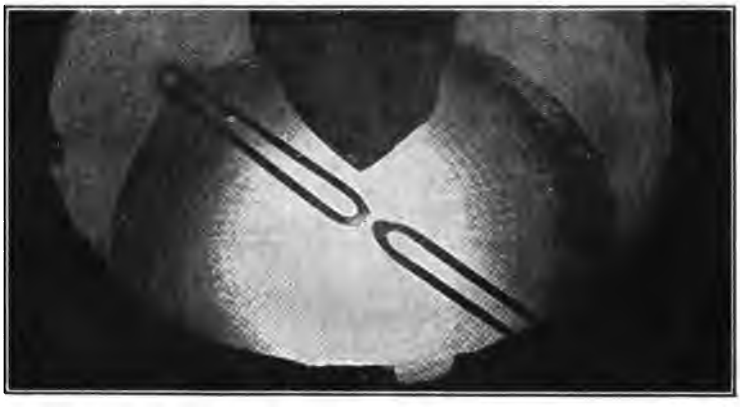


Fig. 23. Thready Arc Furnace.

ally migrate outwards by means of a magnetic field (Fig. 23A). At the outer limit of resistance they break, and are continually renewed in the center. On the passage of a current of air through the flame zone thus produced, oxygen and nitrogen are found to

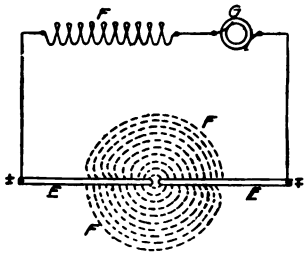


Fig. 23A. Diagram of Thready Arc Furnace.

unite, and, if rapidly removed and cooled, a certain percentage of nitrogen remains thus chemically fixed. Valuable nitrate products are produced from the acids so formed. This process (the Birkeland-Eyde process) has already been extensively applied in Norway and appears to be one of the rare instances of

a successful patented improvement obtaining early recognition and almost instantaneous success. The field of its application is so large, too, that a very important future may be predicted for this manufacture, and for others, which will almost certainly arise, along similar lines, or at least having a similar object.

The above six figures illustrate practical principles of applying the current to *heating purposes*, which cover nearly the whole field of modern electrothermal industries. Many modified forms of each type of apparatus have been employed, and a still greater number suggested, or patented without yet reaching the stage of a practical trial.

The drawback to the development of such schemes for heat application in metallurgical practice has hitherto lain in the fact that, unit for unit, electrical heat has cost from five times to ten (or even twenty) times as much as heat produced direct from fuel.

The reverse of this objection, however, lies in the fact that in many electrical furnaces nearly all the heat produced can be utilized to do useful work; whereas with direct fuel consumption only a small proportion can be so used, because much is carried away by the products of combustion, which must be continually removed. Also, it is often necessary to separate the charge from the fire and the furnace gases, and this involves both a serious loss of heat and a troublesome construction of furnace, as the heat must then all pass to the charge through refractory and badly conducting walls of retorts or muffles or thick iron pans.

These drawbacks to the process of direct heating, coupled with the great reduction which has lately been realized in the cost of electrical energy in some localities, have brought electrical heating in the present day to the verge of serious competition with coal heating, and electric smelting with direct smelting processes. The latter are of course conducted at the coal fields, and connected by rail to the markets, and the former established at good water-power sites, situated on deep water, for shipping the products and raw materials to and from the markets. This competition nowadays bids fair to become serious. I am certainly of the opinion that, with the aid of cheap water powers, electrothermal processes are destined to an expansion and development at present little dreamed of by more conservative minds.

The great advantages offered by electrical apparatus and processes over the older appliances and methods of heating (by means of fuel) will be manifest on very little consideration. First, very high temperatures can be obtained — temperatures which are (even theoretically) excluded by fuel combustion methods; secondly, the heat can be all concentrated at any desired point or limited area, or it can be spread out over any wider area uniformly at will. As no necessity exists for getting rid of large volumes of products of combustion, or supplying fresh fuel (as, for instance, in the case of the ordinary blast furnace), the economy of the electric smelting furnace is mainly limited by the cost of the heat unit and the degree of heat insulation attained. These advantages, and other advantages of construction too numerous to detail, have all the elements of revolution in them, as against the older methods. The opposing influence, as already stated, has hitherto been (and in a certain measure must always be) the greater cost per unit of electrically produced heat than of heat produced by direct combustion of fuel. By reason of this greater cost (a difference which has, however, now been very greatly reduced) it is an essential condition of good design in all electric furnaces that heat losses, by radiation, convection, and conduction, shall be reduced to a minimum; and that where secondary appliances can be conveniently devised for such a purpose the electric heat shall be supplemented by heat produced by direct combustion of fuel. This latter condition is typically fulfilled in a very advantageous and beautiful manner in the case of Héroult's recent patent on the iron smelting furnace, where the CO gas, disengaged in the reduction of iron ore by carbon, is oxidized by a jet of air a little further on, and the heat so produced is utilized to partially heat up the descending charge ready for the final heat of the "arc."

II.

Electrolytic processes. When the effect of the electric current is to be, either wholly or in any large part, electrolytic, continuous currents are necessary. As it is inconvenient to employ a very large number of separate pieces of apparatus, and as each apparatus usually requires quite a small voltage, the current must be generated at very low voltage from the beginning

(which is not economical or convenient from the point of view of the constructor of generating machinery and leads), or alternatively, a rather troublesome and costly element must be introduced, in the form of continuous-current transformers, or rectifiers. This condition adds to the cost of the generating plant, and also to the cost of upkeep of electrolytic as against electrothermal processes. The largest item of expense in the upkeep of such a plant, actuated by cheap water power, being the labor of attention and cost of renewals for the brushes or collectors, it follows that the higher the total voltage that can be employed, the greater will be the economy on this item. Carbon collectors are now universally employed on heavy, continuous-current machines; and modern engineering practice has so far improved the generating machines as to make it customary for makers to guarantee that their machines shall be *sparkless* and efficient at *all* loads. This condition, together with an ample capacity to safely carry *excess* loads, *either* in voltage *or* in current (20 per cent for six hours with 50° C. max. temperature rise, and 90 per cent to 95 per cent total efficiency is a good specification), should be insisted on for all electrolytic work. The extra cost of good and sufficiently large machinery will be found to be more than compensated by the reduction of cost of upkeep and cost of stoppages, which always occur on long runs if the machinery is overtaxed or defective. On the other hand, unlike most other electric installations, it is no necessary part of true economy in electrolytic installations to provide duplicate or spare generating machinery for the purpose of tiding over rare and temporary stoppages. The maximum of economic conditions of such works will usually be found to demand a continuous maximum output from every unit of a given plant; and hence the tendency is *always* to force the generating plant, and "overload" troubles are very frequent occurrences, unless proper provision has been made to meet these conditions.

When the current for continuous-current work has to be transmitted to any considerable distances the machinery is still more expensive. For in that case, to the ordinary cost of transmission must be added the somewhat costly converter, or motor-generator, consisting of a motor attached to a full-sized generator of like capacity (or the two machines combined in one by means of combined windings). This converter must

always be arranged near the furnaces (or cells), in order to economize the heavy conductors, and must be provided with separate instrument boards, etc. When long-distance transmissions are undertaken it will usually be found best to employ an alternating three-phase primary current, actuating on one-shaft low-tension direct-current converting devices (rectifiers). In some instances aluminium rectifiers may be employed or separate motor-generators in others.

Like the thermal furnaces the apparatus used for electrolysis may be illustrated by a few leading types. The following six cuts illustrate general principles.

Fig. 24 shows the typical arrangement of the anodes and cathodes employed wherever a vat or tank containing solutions

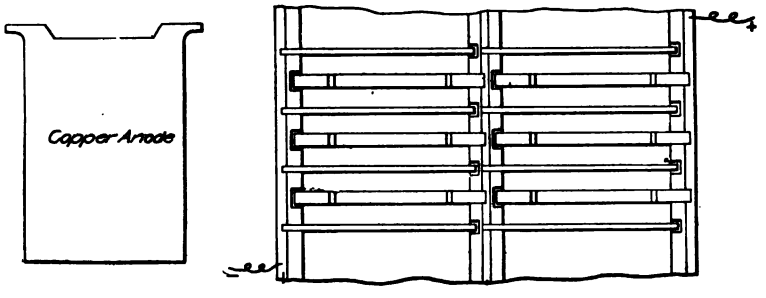


Fig. 24. Copper Vat.

has to be stocked with plates carrying heavy currents and separated by only narrow widths of any solution. The oldest and most typical operation of this nature is copper refining. A similar vat and arrangement of electrodes has been employed in zinc recovery and in lead refining and also in some other industries.

Fig. 25 shows an apparatus for use with fused electrolytes and carbon anodes, which are consumed during the electrolysis. It is the type of vat used in British works for aluminium production from purified bauxite. The liquid aluminium cathode lies on the bottom, and the current is led in by a plate of iron over which a plastic carbon lining has been previously stamped and baked. The anodes are adjustable by screws supported on a bronze omnibus bar. The electrolyte of fused cryolite and

alumina is covered over with a layer of carbon to prevent loss of heat and lessen the glare from the vat, and the useless consumption of the anodes by atmospheric oxygen. The metal is periodically tapped from a tap hole. Very heavy currents are employed (about 2,000 amperes per anode of 10 in. × 10 in. dimensions)

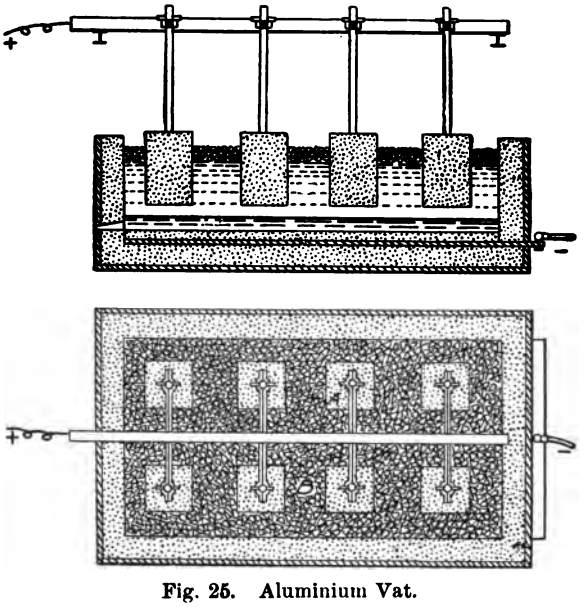


Fig. 25. Aluminium Vat.

and only a few volts, — 4 to 7. The CO_2 gas formed diffuses in the air, being in too small quantities to be harmful.

Fig. 26 shows another form of fused electrolytic apparatus. The special features about it are that the carbon anodes are not consumed, the gases produced are confined and utilized, and the liquid cathode is continuously and automatically tapped into a side pocket. This apparatus is used for electrolyzing zinc chloride in admixture with sodium chloride, obtaining zinc and chlorine. The lining is ordinary silicious brick or fire clay. Quite large currents may be employed (from 1,000 to 10,000 amperes), and the voltage ranges from 3 to 7, according to size of apparatus, the critical voltage of reaction being 2.2 and the balance being employed in maintaining the charge fused.

Fig. 27 is a very specialized form of apparatus for fused electrolysis, called a sodium pot. It is the cell used for produc-

tion of metal sodium by the Castner process. The electrolyte is pure, fused caustic soda, and the anode and cathode are of nickel and copper respectively. The outer vessel is of iron, and the bath is kept fused by the current.

An apparatus for electrolyzing solutions of common salt, with a moving mercury cathode and a double electrolytic cell (wherein the cathode products of one cell are conveyed into the next

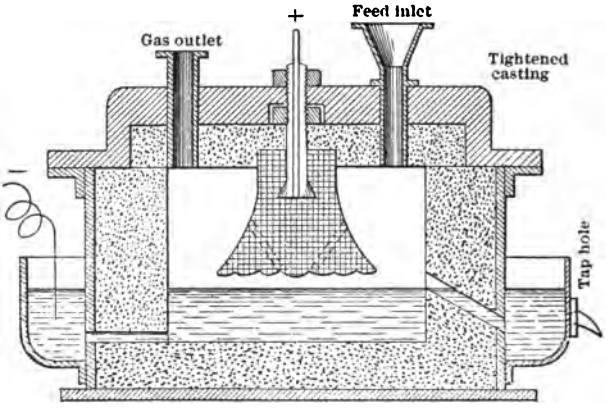


Fig. 26. Fused Zinc Chlorine Vat.

compartment and there become subjected to anode influences), is typically illustrated in Fig. 28. This form of cell is also a very specialized apparatus, which has found extensive commercial application for the manufacture of chlorine and caustic soda. It is notable, however, as an instance of curious industrial histories, that, for that particular purpose, the root and at first sight most attractive idea of the Castner invention, viz., the passage of the same current in the second cell to promote anodic influences on the products of the first cell, is found to be neither necessary nor useful. The Castner process as actually carried on commercially for all practical purposes has the second cell short-circuited and is, in fact, a reversion to an older process (Nobles and Sindingharsen's patents). The commercial success of Castner's process is due in this case as in some others, not to the original invention, which in fact proved unworkable, but to the stimulus which the supposed possession of a valuable monopoly gave to the practical development of the industry in capable

hands. I shall refer to this matter at greater length when dealing with the element sodium and its derivatives, but it has now a purely historical interest, as the original Castner patents have all or nearly all expired, and everyone gladly recognizes the great

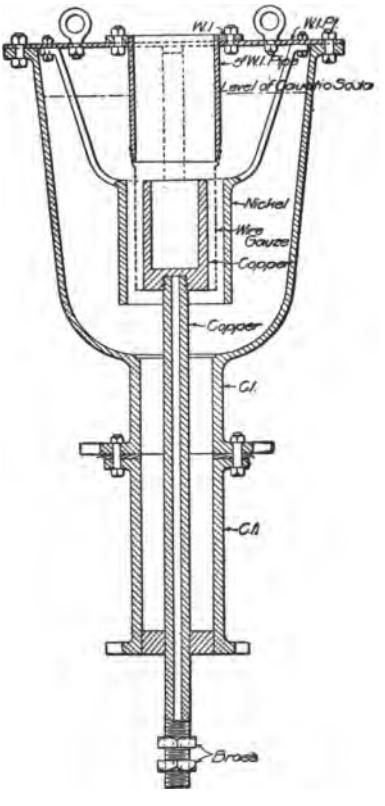


Fig. 27. Sodium Cell for Fused Caustic.

merits of the process for which Castner secured by his labors a large commercial application.

Fig. 29 shows a type of solution apparatus making only gaseous products. It is the Schuckert cell for the commercial electrolysis of water into oxygen and hydrogen gases.

These six general types of apparatus practically cover the whole ground of electrolytic industries as at present practiced; although of course there are a great many varieties of each type

designed for application to a great many varieties of special purposes. These will be described in detail and illustrated under their respective headings when dealing with the elements alphabetically.

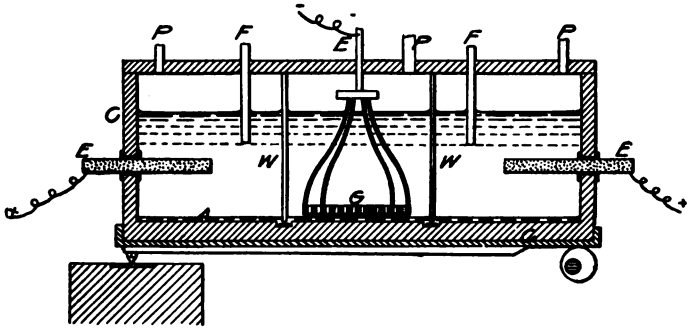


Fig. 28. Mercury Caustic and Chlorine Cell.

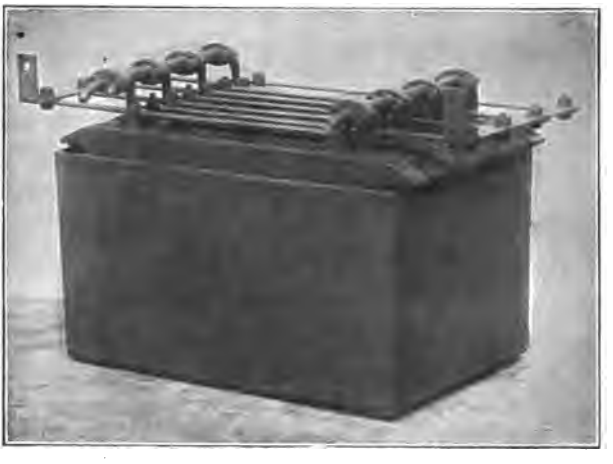


Fig. 29. Gas Cell.

III.

The cost of conductors is a very heavy item in the capital cost of all electrolytic or electrothermal work, and in all such practical applications of the above principles to commercial uses a consideration of the very first importance, if a plant is to be well designed and economical, will be to so arrange it as to

secure a minimum quantity of idle conductors, whilst still allowing sufficient room all round the apparatus to properly reach and attend to all the parts, and perform the various feeding and tapping operations conveniently. For this reason generators (primary or secondary) from which the working current is drawn, are usually placed in a building adjoining the vat (or furnace) room, and are separated only by a wall of sufficient thickness to prevent fumes or dust from passing from the latter to the generator. The raw material, or liquid supplies, are usually introduced at the other end of the vat room or furnace room. This general design for electrolytic or metallurgical plants is almost universal, and is illustrated in diagram in Fig. 30. It will be seen that it also has the advantage that it permits of progressively extending the size of the works by separate units added laterally. A large part of all such works will usually consist of accessory apparatus for the treatment of solutions, etc.

For the same reason the ordinary conditions of an electric (power and light) generating station, where the current is first taken to a distributing board, and thence to the mains and apparatus, may with advantage be modified when electrolytic operations are intended. All the arrangements should be designed with a view to eliminating any considerable lengths of heavy conductors from the circuits wherever possible.

The measurement of heavy currents such as are used in electrolytic, or electrothermal, operations is now universally accomplished by a system of shunts and millivoltmeters (a modified form of the old potentiometer principle). A short length of platinoid, of carefully calibrated resistance, is introduced into the main circuit and this so-called "shunt" is provided with two terminals, from which smaller wires (also of calibrated resistance) lead to the actual indicator, which then consists of a millivoltmeter with suitably calibrated scale, to read the current directly in amperes. By this admirable system (the arrangement is illustrated in Fig. 31) any strength of current can be quite conveniently measured, and the dials or recorders can be placed in any handy position — a condition which it would be extremely troublesome to fulfil, were it necessary, as in the older devices, to lead the heavy currents though the instruments themselves, when placed on the switchboard. The

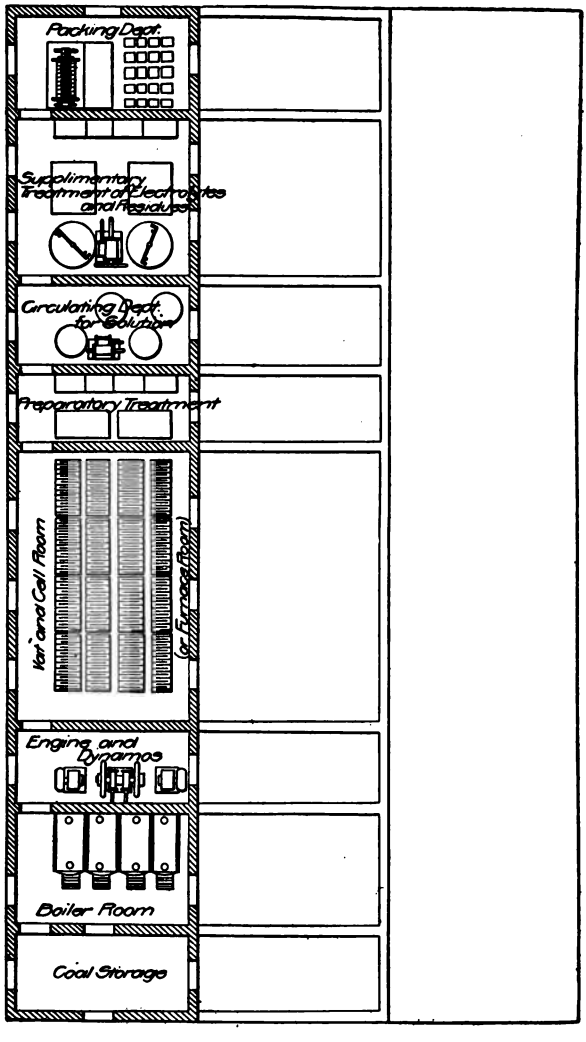


Fig. 30. Typical General Design of Electrolytic Plant.

measurement of voltage is, of course, a simpler matter, and may be carried out by the Weston standards, or by any other system of direct reading, and suitably calibrated instruments.

Every well-designed plant should be provided, at the secondary generating station, with large-dial current and voltage indicators for each machine, and also with recording volt and ampere instruments of good quality for each circuit. Also most processes will be the better for a number of low-reading voltmeters, which may,

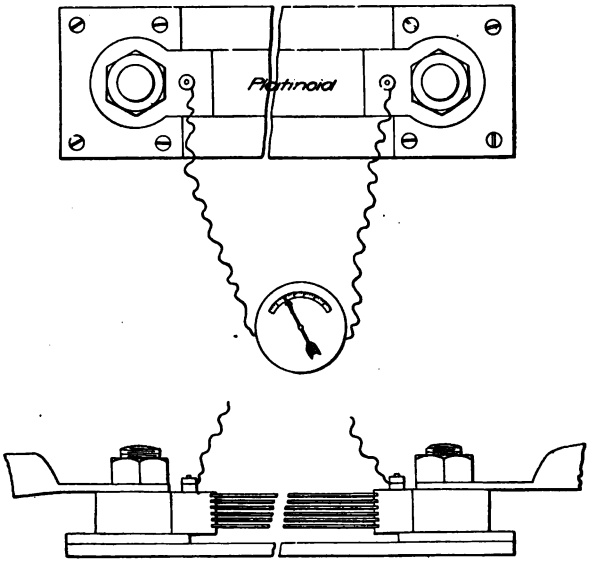


Fig. 31. Shunt Method for Measuring Current.

however, be of somewhat cheaper and rougher quality. When these are fixed at the terminals of each line of vats or furnaces, and so subjected to much wear and tear, through irregular action (and often also directly on each electrolytic apparatus, where they must be very numerous by reason of the large number of separate cells usually required), they usually take some specially cheap form. Thus, in aluminium deposition by the Hall process, a 20-volt incandescent lamp is used. It shows nearly black at the normal voltage (7 volts), but when the dissolved alumina is exhausted from the cryolite bath, the voltage rises and may even reach 25 volts. The lamp then lights up brilliantly, and the workman knows that more alumina is required in the bath. In

similar way, in large installations, a system of electric bells and indicators is usually employed between the terminals of copper-depositing vats, and is so arranged as to ring the bell in case of a short circuit and indicate the particular vat where it occurs. Ackers, in his fused salt electrolysis, used a simple magnetic compass needle, hanging pivoted on the main conductor bar leading to each separate anode (there are 4 anodes to a cell). The behavior of this needle serves as a rough indication to the workman of the amount of current flowing in that particular anode, and assists in showing what adjustments are needed. A voltmeter, reading from 6 to 25 volts, is also employed in this case on each cell.

A test very commonly resorted to by the workmen in such plants is to simply feel the warmth of any exposed length of conductor. It is fairly easy for a practical hand to become familiar with the temperature and so to gauge the current flowing by this means within sufficiently narrow limits of accuracy for many practical purposes. This puts one in mind of the time-honored cook's practice, — feeling the handle of the oven door. All such works' "dodges" are in fact the natural and certain outcome of experience in each case coupled with any ordinary degree of ingenuity.

In operations such as we are considering, the necessity of measuring temperatures with as great a degree of accuracy as possible very frequently arises. For all temperatures below 200° C. simple mercury (glass) thermometers are manufactured very cheaply, and can scarcely be improved upon for general use. For temperatures between 200 and 550° C. a special form of mercury thermometer with nitrogen atmosphere is manufactured, and for laboratory uses is often quite satisfactory. For works' use it cannot, however, be recommended, as it is both expensive and extremely fragile. Glass thermometers are also quite unsuited for use with such substances as fused caustics, fluorides, etc. In all such cases, either one of the more expensive and older forms of pyrometer (Le Chatelier, etc., which acts through variations of the resistance of a long platinum wire at varying temperatures and is very accurate and quite easy of application) may be employed; or for most purposes of a works' requirements the newly invented and much cheaper (Bristol) pyrometer, which acts on a thermo-electric principle, may be used. The latter is

reasonably cheap and quite effective, and its introduction bids fair to adequately fill a much felt need. There are now many makers of such instruments.

The selection of suitable materials and suitable designs for pumps, pipes, agitators, vats, fitter-presses, and every possible variety of apparatus, forms a very large part of the necessary power of judgment and necessary equipment of specialized knowledge of the practical engineer engaged in these industries. The problems involved, however, are very largely the same as those encountered in ordinary chemical engineering, and need not therefore be further discussed here.

The question of buildings and housings for plant is in very much the same category. All the problems which the designing engineer is confronted with are very much the same as in the construction of buildings for other chemical or metallurgical operations. The relative cost of various materials; the local material and labor supplies and habits; the peculiarities of the country, and especially of the climate and the requirements of ventilation, — have all to be taken into consideration in selecting the most suitable, and at the same time the most economical, types of housing. It may be stated as a general principle that the buildings required for electrolytic or electrothermal works can usually be, with advantage, selected of a more permanent character than those for most other works of a chemical or metallurgical nature. Some of the German plants and a few of the English ones have very fine buildings indeed, and those at Niagara Falls and at other American centers of industry are occasionally very good.

IV.

I will conclude this chapter with a few illustrations of a typical character showing in general plan the arrangement of some modern plants of large size. These are illustrated from designs adopted in many different countries and are intended to be only broadly representative.

Fig. 32 shows a large aluminium plant (Scottish) operated by water power and employing about 7,000 h.p.

Fig. 33 shows a large alkali and bleach plant (English) employing about 7,000 h.p. and operated by steam engines, whose

boilers are fired by Mond gas. The generating plant is now being slowly converted to gas-driven engines.

Fig. 34 shows a large zinc works (projected only) for use of some 5,000 h.p. on a sloping hillside at a Norwegian waterfall.

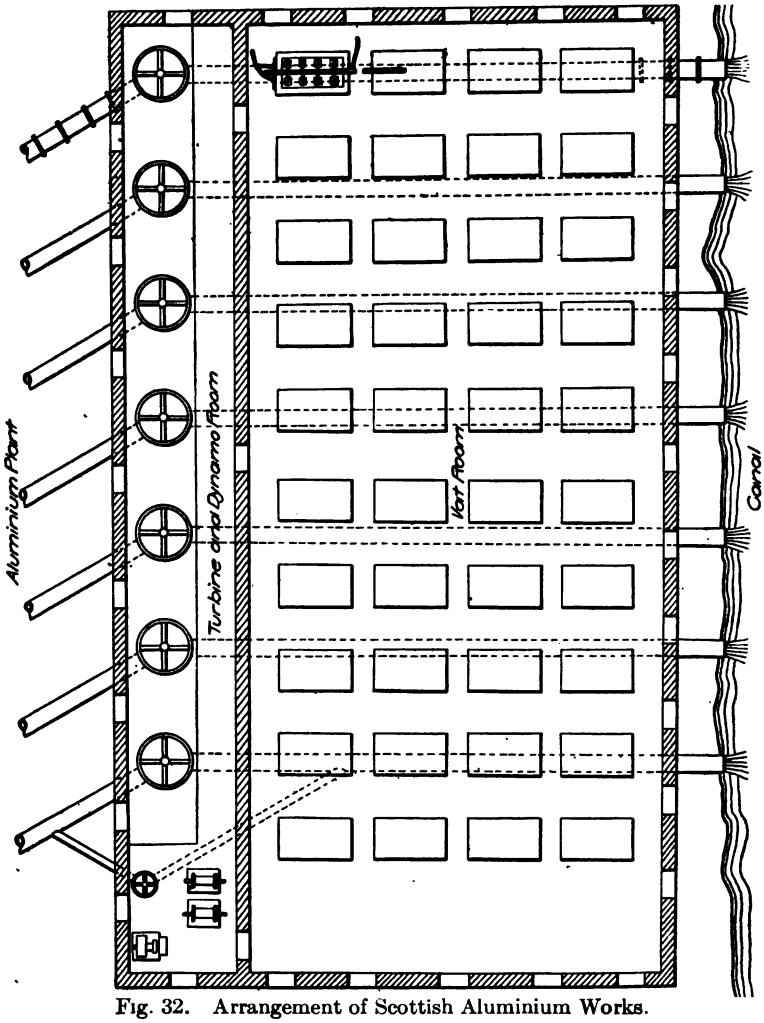


Fig. 32. Arrangement of Scottish Aluminium Works.

Figs. 35 to 37 are illustrations of special supplementary devices peculiar to these industries, which will also be of interest.

Fig. 35 shows the mode adopted at a large modern works of

conveying the electricity into and out of such apparatus as the carbide furnace.

Fig. 36 represents the mode of conveying electricity into and out of the aluminium furnace (Héroult).

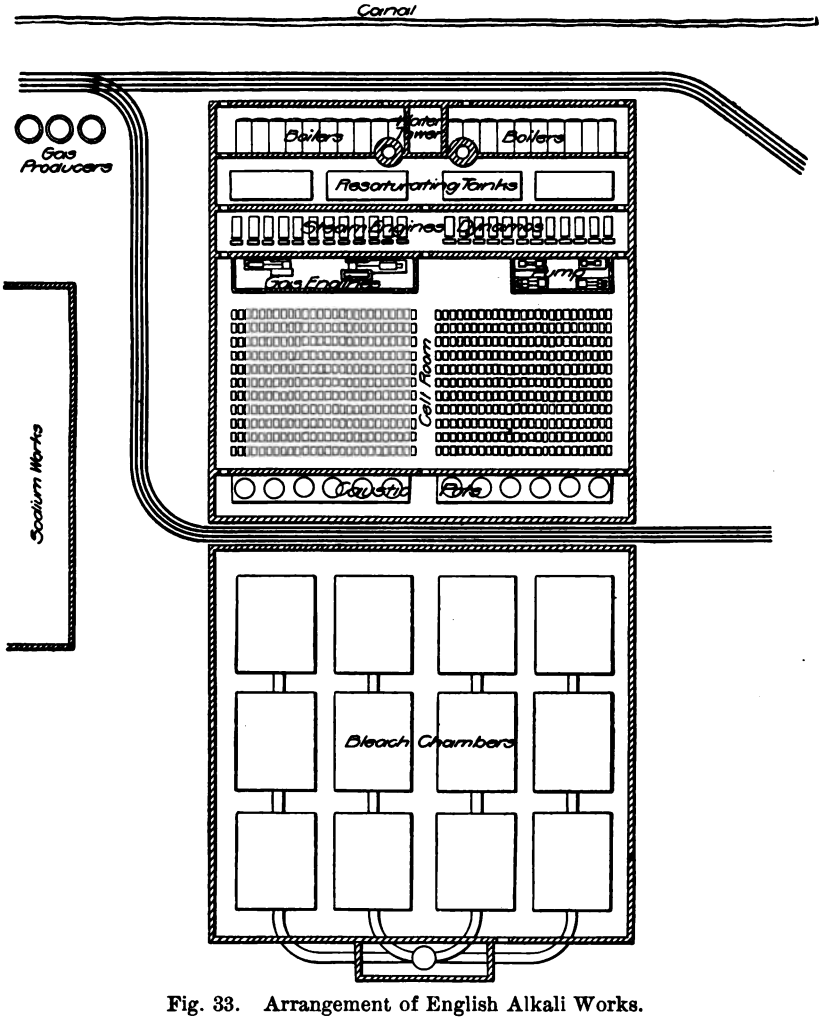


Fig. 33. Arrangement of English Alkali Works.

Fig. 37 illustrates the mode of magnetically circulating the charge in a fused sodium chloride vat (Ashcroft system).

The most noticeable general features of all electro-chemical

works when compared with the works of the older chemical or metallurgical processes are two. One is the extreme smoothness, cleanliness, completeness, and ease with which the operations are carried on; also the comparative absence of the enormous waste heaps (of slags and other by-products) which so largely characterize and disfigure all smelting works and the older alkali works. The second general feature is not so favor-

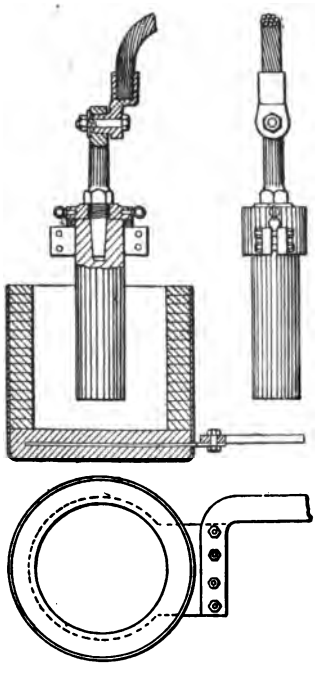


Fig. 35. Connections to Carbide Furnace.

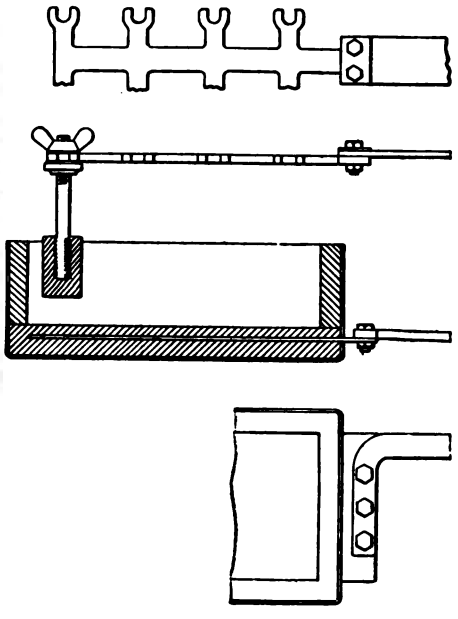
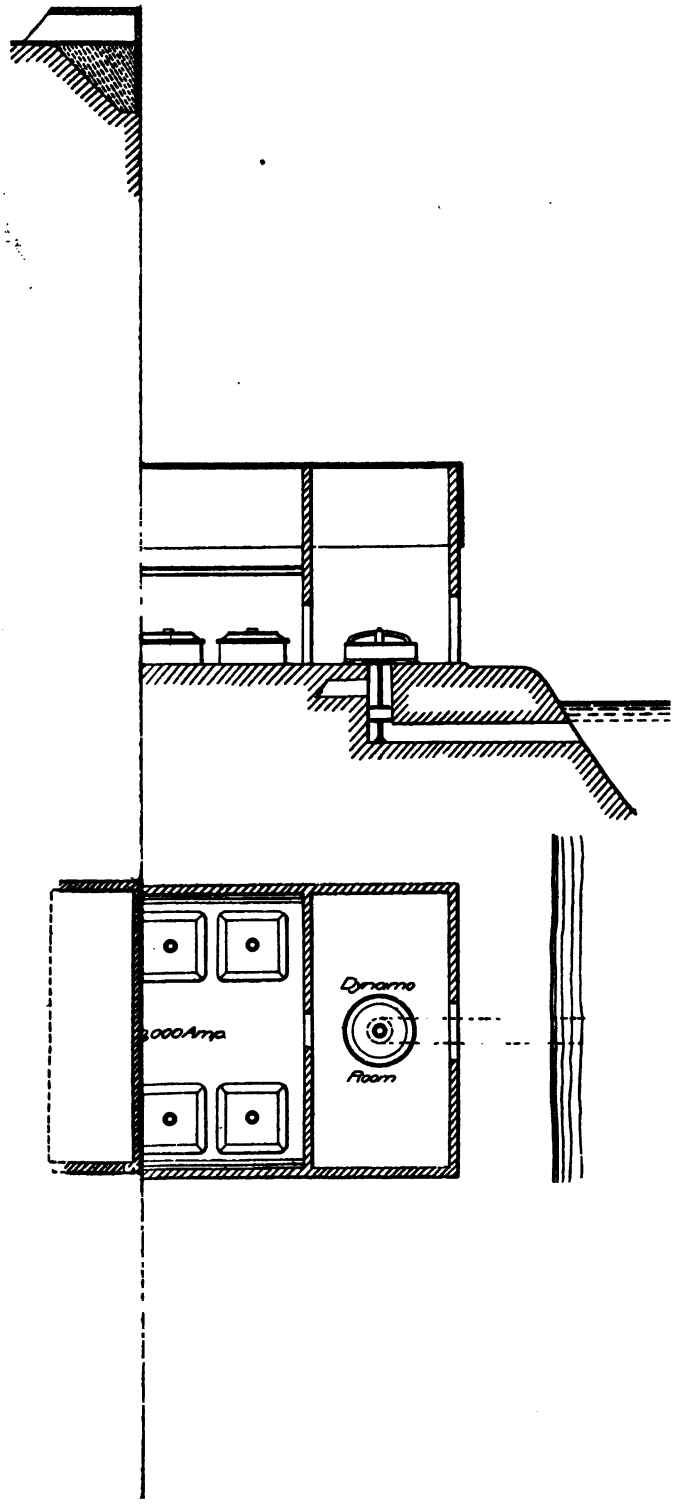


Fig. 36. Connections to Aluminium Furnace.

able. It is the enormous extent, intricacy, delicacy, and costliness of the apparatus required to produce a given result by the electrical methods as against the older methods.

It is in consequence of this last mentioned feature, in fact, — a feature which seems inseparable from electrical processes, — that the growth of the industries we are considering has not been quicker than it actually has been, for there is now no doubt that electrical methods can be employed, in a large number of instances, to replace older chemical and metallurgical


Dynamo
Room


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operations, and that the electrical methods possess many advantages, including economy of working, in most instances.

The further growth of these methods, therefore, seems limited principally by the factor of capital cost; and in all cost sheets

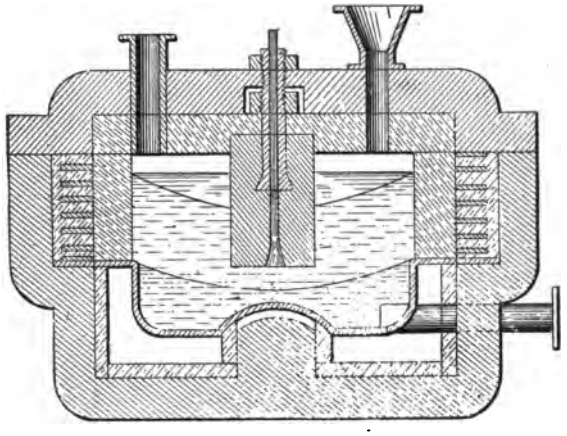


Fig. 37. Fused Sodium Chloride Vat.

for such processes the various items of capital charges loom very large. At least half of the total capital, however (sometimes three-fourths), is involved in the power plant. Therefore the governing feature of preponderant influence on the future will clearly be cheap power in suitable localities. And this leads me naturally to the subject of the next chapter.

CHAPTER VI.

PRODUCTION OF CHEAP ELECTRICAL ENERGY.[1]

THE industries of electro-metallurgy and electro-chemistry became commercial only with the invention of the dynamo in 1867. In the following years, the rapid improvements in this machine, and in the steam engine and gas engine, were the signal for the simultaneous appearance, and extraordinarily rapid expansion, in a small way, of all kinds of electrical processes. During barely a quarter of a century, since it became fairly started, this growth has been phenomenal.

And to-day we are standing on the verge of very much greater developments. This, I think, is not mere conjecture. Its actuality is nearer than many suppose, and is foreshadowed by such events as the recent experiments in the electric smelting of iron, the developments in steel refining, the success of the nitrogen works at Notodden, in Norway, the introduction of a successful lead-refining process, sulphide ore experiments, lead and copper smelting experiments and projects, zinc distillation, and many other promising operations just emerging from the experimental stage.

It is becoming clearer every year, that the actual extent of these developments will depend mainly on the practical limits to which the cost of electric energy can be reduced at suitable sites. Those who are capable of taking a far-sighted view of commercial prospects now begin to realize that the whole industry will depend for its most extensive future progress, very largely, upon the thoroughness with which this fundamental fact is recognized by technical and commercial men.

Errors have already been made, sometimes on a very large scale, from failure to appreciate this broad governing aspect of the case. Expensive steam plants have been erected, to generate power for industries which cannot, legitimately, afford the cost

[1] Extracts from this chapter have appeared as a paper read by the author before the Faraday Society, November, 1908.

of steam energy at all; a few years later, on discovering the disadvantages they labored under, such plants have been (again expensively) equipped with gas engines. But still the cost of energy has proved too high.

The large developments of the last ten years at Niagara Falls have familiarized the world, in a general way, with the possibilities of water power; but they have also brought certain well-defined limitations to light, for it now becomes evident that still cheaper energy than Niagara Falls can afford, under any conditions likely to arise, will be demanded for certain very large, technically possible, industries if they are to become commercially possible on electrical lines.

What, then, is possible? Let us examine the problem from the commercial side. The cost of electrical energy depends on three principal factors: (1) fuel, (2) operating expenses and upkeep of plant, and (3) rents, royalties, interest, and depreciation (or, broadly, capital charges). It is customary to consider rents or royalties separately, and to estimate the interest and depreciation charges taken together at say 10 per cent of the total cost of construction. This figure is certainly not too high to include the necessary sinking funds, to provide for changes in types of machinery, which often occur at comparatively short intervals in a new and developing industry, and also to pay a proper return on the money invested as debentures, or secured capital.

When independent capital is employed in the development of the power (as in the case of the Niagara supply companies), a higher rate of profit must also be allowed for on the capital invested. But in the case of Niagara, there are no proprietary royalties. There has, as everyone knows, been a great deal of talk about, and much outcry against, the Niagara supply companies. On the one hand, the sentiment of the public objects to the feared extensive destruction of the falls; on the other hand, excessive profits are alleged. I do not know what are the actual working costs of these supply companies, and I have only general statements of their capital outlays before me. But it is easy to form an approximate comparison between the conditions there and elsewhere, and I know that both items — working-costs and capital — must be considerable, especially the latter; I am also certain, from calculations I have made, and from a clear perception of the general principles involved, that these com-

panies are not making any very excessive profit out of energy sold at the lower rates charged to the electro-chemical producers, whatever they may reap out of their long-distance lines, from energy sold for lighting or factory power purposes. A similar amount of capital and intelligence embarked in many other industries (even if the enterprise be considered as a whole) would in fact earn far higher rates of interest.

And yet the price is not low enough to satisfy the rigid economical demands of such processes as electric iron smelting, nitrogen fixation, and sulphide ore treatment, to say nothing of other possibilities, such as copper smelting, lead smelting, zinc smelting, distillation, etc., which would soon become commercially possible with still cheaper energy. The only possible way to reduce the prices at Niagara to a suitable limit for such industrial operations, would be to erect generating plant and development works on which much lower capital charges were incurred. Such a scheme might be possible if the famous "Goat Island" were given over to destruction, and plant erected there capable of generating electricity directly from the falls with very short tunnels for tail-races, etc., and utilizing the power drawn from low-tension generators on the spot. But it is safe to predict that such a scheme will never be projected and sanctioned, for public sentiment will forbid it, and I do not think that many people wish it otherwise.

But if this power at Niagara is too dear, what chances have the steam engine, the gas engine, and the oil engine — forms of energy production which one hears so much about nowadays? As main generators of electric energy for the purposes above stated, I answer at once that they have no chance at all; for, even if absolutely free and regular supplies of fuel were available for such engines (which is certainly not the case), the capital charges and the upkeep would still bring the cost of the unit of electricity somewhere about the level of the Niagara prices, and still far above the "low-grade limit" which will be inexorably demanded by the coming new industries as a root condition of their being.

I should be inclined to suggest for this "low-grade limit" about \$10 per kilowatt-year (= \$7.50 per electrical horse-power-year), and we may at once quite safely assume that no means of producing energy at present known or thought of can

touch this limit, except one, and that I have designated water-powers of Class 1.[1]

In suggesting this limit, I, of course, assume that some profit is to be made on the large industries considered, not merely the covering of working expenses. The undeveloped water-powers of the world, as yet, are very numerous, and as a consequence no regular market value has yet been placed upon them in public estimation (except in special circumstances where their open market is at once apparent). I have treated the possibilities of royalty payments as a contingent item in the comparison of costs. This item will, however, find its natural commercial level as the industry extends and the demand for such water-power increases.

The following table of comparative cost of the various available means of producing energy is prepared from many records, and it aims at striking a useful average. Of course it follows without saying that no average price can be quite accurate for all countries, but nevertheless the difference in these figures in different situations is not in fact so great as might at first appear likely, when the division of water-powers into two classes is adopted. The principal difference will be found to be a striking and fundamental advantage peculiar to water-powers of Class 1.

I do not propose to discuss at length either steam, gas, or oil engines here, for a glance at the table shows that they are quite out of court in this larger connection which we are discussing. The best practical source of power to-day is the favorably placed waterfall; the next best is the water-power of Class II, which may also sometimes have the advantage of being obtainable nearer home.

When it is considered that the scope of the oil engine is necessarily limited, and that even with fuel quite free, the gas engine and its generating plant are handicapped with capital charges which alone are more than double the entire working costs and royalties of the water-powers of Class 1; and upkeep charges which are also very heavy (and cannot by any apparent possibility be greatly reduced), — it should be at once evident that there can be no real competition in the coming future

[1] That is to say, those in which favorable natural conditions enable the development of the power at a very low expenditure of capital.

between these two methods of producing electricity for use in the great bulk of electrolytic and electro-thermal production. However favorably the gas engine and the oil engine may be looked upon for a time, and during the transition stages of the industry, these generators cannot compete in any equal sense with the best water powers as prime motors for the work we are discussing.

TABLE 6. — RELATIVE COSTS OF ELECTRICITY PRODUCED FROM STEAM, GAS, OIL, WATER (2), AND WATER (1) FOR CONTINUOUS LOADS.

Item.	Steam Engines		Gas Engines.		Oil Engines.	
	Per Kw. Year.	Per H.P. Year.	Per Kw. Year.[1]	Per E.H.P Year.	Per Kw. Year.	Per E.H.P Year.
Fuel	$20.63	$15.75	$12.00	$ 8.50	$20.00	$15.00
Labor	2.75	2.00	2.00	1.50	1.75	1.25
Upkeep	3.25	2.50	4.00	3.00	4.00	3.00
Capital charges	15.00	12.13	16.50	13.25	10.25	7.75
Royalties on rights	.....	.....	.....	.....	.....	.....
	$41.63	$32.38	$34.50	$26.25	$36.00	$27.00

Item.	Water, Class 2.		Water, Class 1.	
	Per Kw. Year.	Per H.P. Year.	Per Kw. Year.	Per H.P. Year.
Fuel	.....	.....	.....	.....
Labor	$ 2.00	$ 1.50	$ 1.50	$1.00
Upkeep	3.25	2.50	2.00	1.50
Capital charges	20.50	15.50	3.25	2.50
Royalties on rights	.75	.50	3.25	2.50
	$26.50	$20.00	$10.00	$7.50

[1] Varies greatly according to value of by products.

A large and growing demand for gas engines, however, is indicated by the state of the markets to-day, a circumstance which is explained by the fact that many operations consuming energy are absolutely bound to be carried out at spots

where no water-power can be obtained. Moreover, in the particular industries which I am considering here, quite a large demand may yet arise for gas and oil engines; for there are indications of a tendency to devise apparatus wherein a combined use is made of electrothermal (orelect rolytic) and of direct combustion principles. Thus it has been suggested that a charge of iron ore, carbide materials, or similar raw material, might be heated up by ordinary fuel combustion to nearly the required temperature, and made thus to imbibe a large number of heat units at a cheap rate, and then finished off by raising it to final temperatures, with the aid of the more expensive electric heat. Such operations could of course be carried on economically at sites even nearer to the markets than the cheap water-power sites, of which I shall speak presently, and an advantage of some importance may often be thus obtained in respect of freights.

In such countries, too, as England and Germany, where there are few or no water-powers of Class 1, there will be found a great desire to keep all industrial operations as much as possible within the respective countries. For these reasons the gas engine has every chance of encouragement. But the fundamental and unalterable natural economic conditions of any industry should not be allowed to become wholly obscured by such considerations. I am convinced that very much larger developments will take place during the next few decades at the first-class water-power sites. Such developments, in fact, will only be limited by the comparative scarcity of this class of power in the world; and I may add by the suicidal and false patriotic ideals of the peoples of the few naturally favored lands where such powers exist. I regard it as probable that when such people as the Norwegians discern how foolish has been their exclusive policy (and there is no people more eager of gain when their cupidity has been aroused) there will be a complete reversal of the present exclusive policies, and foreign capital not only will be welcomed, but encouraged (or even subsidized) to develop the natural resources of the country. When this takes place I predict for these industries and for the few fortunate lands which possess the water-powers of Class 1, and so will be able to eventually capture the bulk of them, an immense access of prosperity.

In support of this belief the following significant figures may be cited. Although electrically produced heat can probably never actually compete in cost, unit for unit, with coal purchased and burned direct, yet the ratio of cost between the two is, even now, much lower than is usually supposed, whilst the ratio of "efficiency" brings the two still more nearly on a level, turning the scale in many cases in favor of greater economy for electrical heating.

One pound of an ordinary quality of coal will produce, if burned in a producer, and supplied to a modern gas engine, about one electrical horsepower-hour, and it will cost at the pit's mouth (at $2 per ton) 0.1 cent.

This amount of electric energy (one electrical horsepower-hour) is equal to 644,544 gram-calories of heat energy.

Burned directly to generate heat, one pound of coal will produce approximately 3,000,000 gram-calories. Therefore, by burning coal, for one dollar we may procure a theoretical combustion heat of approximately 3,000,000,000 calories.

The same dollar employed in purchasing electrical energy at the cheapest rate (Class 1, water) yields one electrical horsepower for 1,168 hours, and is therefore equivalent to 752,827,392 calories. This is just about one quarter of the yield from direct combustion of an equivalent value of coal.

It may be safely assumed that the labor and wear and tear of furnaces if taken together will be about equal in each case.

The heat produced electrically can, however, be much more usefully employed, so that a true comparison of the cost of heating processes by the two methods can only be made in the full light of experimental data, determining the "efficiency" of each furnace or special apparatus.

When it is remembered that the "efficiency" of many non-electric furnaces is barely 10 per cent of the theoretical, and very few will exceed 25 per cent, whilst the efficiency of electric appliances sometimes reaches 75 per cent, and is often 50 per cent, it will be seen how closely this cheap power of to-day is competing with fuel combustion, even as a mere source of heat for metallurgical or chemical reductions. A class of work for which an immense amount of coal is now burned annually could therefore in the future be largely performed by electrical methods, and one of the recognized menaces of the future (the

exhaustion of the world's coal supplies) be thus considerably mitigated.

In the case of water-power a great deal of variability exists as to the possibilities of economy. The actual cost of labor and upkeep for a modern generating plant, actuated by water-power with good machinery and untroubled by any irregularities of working, may be easily reduced to a perfectly nominal sum (about $1 per horse-power-year is sufficient in such cases for any fair sized plant, and with very large plants it may be brought down to half that sum). The gross cost of the power to the consumer then becomes practically dependent on the amount of capital charges (and valuable private rights) involved. These items will vary enormously, according to whether the flow of water is naturally even all the year round, or whether expensive dams must be constructed to regulate it; whether the pipe is long or short, the fall high or low; whether much valuable property is submerged by the dams, and other conditions.

By designating the various water-powers Class 1 and Class 2, I distinguish between those powers where a high cost of regulation or development has been necessary to bring the water to the place of consumption and to insure an even supply all the year round; and those cases where this has been provided, more or less completely, by natural conditions; thus rendering the capital employed much lower.

In general it may be stated that a total capital expenditure of $35 per electrical horse-power capacity is sufficient for the development of powers of Class 1, including all necessaries up to the dynamo terminals; whilst some powers which exist in Western Norway can be developed still more cheaply. On the other hand, water-powers have been developed in Eng'and and in other countries which have cost upwards of $300 per electrical horse-power for harnessing equipment and compensations. The total cost at Niagara Falls cannot have averaged less than $150 per horse-power.

It is needless to say that unless it be undertaken for some very good and exceptional reason, such an expenditure as $300 per horse-power, in the light of our modern understanding of this subject, is quite prohibitive and ought not to be seriously proposed.

In considering the various water-powers available through-

out the world, there are, of course, many stages between these two extremes, and in some of these stages it may be possible to set some royalty value on the water rights. In general, however, it may be assumed that only powers which are strictly of Class 1 will be able to successfully demand high royalty values; and that powers of Class 2 (and intermediate stages) will only be developed in future when some public object is supposed to be served by their employment. The grants for such powers will mostly be free, or nominal royalties only will be charged.

The powers of Class 1 (especially the best ones) are not very numerous, and their enormous natural advantages will to some extent be neutralized by the high prices which will naturally be placed on the water rights by owners when their true values become known, and when a ready market is opened for them. Nevertheless, I believe it is almost exclusively to powers of this type that we must look for the future of such gigantic possible developments as are suggested to-day by the looming processes of electrolytic iron, nitrate production, and the treatment of complex sulphide ores, — three fields of enterprise, any one of which, if successfully developed, must rapidly exceed in magnitude the entire industry of electro-metallurgy as it exists to-day.

As this class of water-power seems destined to play so important a rôle in the near future, it will be of special interest here to give a concrete instance of such a water property and of the method employed for arriving at the capitalized value of the water right. The example is drawn from one of the most favorably situated of the many favorably placed powers in Western Norway where the existence of these sources of energy on the verge of deep water and ice-free harbors, suitable for any kind of shipping, is probably unique, offering advantages to industry found nowhere else in the world in such happy combinations.

The property was acquired about eight years ago, from the former Norwegian owner. The purchaser left some mortgages standing, so that the capital stood as noted below when he succeeded in obtaining title (a royal concession under the foreigners' exclusion acts) to own the property. Extensive surveys had been made, and the engineers had pronounced the waterfall (which had a fall of 1,000 feet, with a very short distance for pipe line from the outlet of the last lake to the lowest level) to be good

for about 7,500 kilowatts, and capable of development for about Kr. 100 ($26.75) per horse-power; which sum was to include also some payments to farmers for fullest damming rights — in fact, it included the purchase of nearly all the farms on the margins of ten miles of lakes, which headed the fall. It also included the cost of damming the principal lakes, at a very favorable spot, whereby, for the comparatively small sum of Kr. 50,000 ($13,375) enough water could be stored in the lakes to completely equalize the fall all the year round and so use every drop of water that falls on the watershed. Though the total area of the watershed was small, the annual rainfall is the highest in Norway, reaching 3,600 m.m. per year. There was, therefore, enough water to ensure an even supply of 3.8 cu. m. per sec. all the year round after liberal deductions for evaporation and loss. The lake basin was large enough to secure complete equalization of the supply. Also the intervals of drought are never very protracted when compared with such intervals in countries like England. All these circumstances are most favorable for cheapest development.

TABLE 7

Showing the influence of the cost of developing a waterfall (and installing machinery) on the capitalized value of the water right, showing also the method of calculating return on capital invested.

The fall has a capacity of ca. 7,500 kw's. It is supposed that a contract (with suitable guarantee) has been obtained for renting 6,000 kw's. at an inclusive charge of $12.50 per kw. year delivered at switchboard (= app. 35 Kroners per E.H.P.-year).

According to estimates and existing contracts the expenditure required will be as follows, viz.:

Earthworks·

Tunnel 300 m. long @ $22.06	$ 6,618	
Intake, masonry, etc.	2,775	
Pipe track leveling	2,775	
Dam at Röervik lake and cuts	27,775	
		$39,943
(N.B.: equal to $6.65 per kw.)		

Buildings: —

One power station, two valve houses, sundry observation boxes, telephone, posts and sluiceman's house		$13,330
(N.B.: equal to $2.22 per kw.)		

Ironwork: —

One pipe line of 800 m. length with all sundries	$31,110	
Sluices for dam, intake and cuts	2,775	
		$33,885
(N.B.: equal to $5.64 per kw.)		

Machinery: —

Pelton wheel turbines, dynamos, and regulators	$63,885	
Transformers and 2 km. line	36,110	
Electrical outfit	5,550	
		$105,545
(N.B.: equal to $17.60 per kw.)		

Special charges and allowances: —

Compensation to farmers, payable on exercise of damming rights as per contracts	$11,100	
Special tax demanded by Herredsstyrer	6,935	
Contingencies on building estimates	11,385	
		$29,420
(N.B.: equal to say $5 per kw.)		
Total development cost as estimated		$222,123
General margin for contingencies		27,775
		$249,898

This expenditure will be provided for by the issue of $166,620 preference shares and $83,278 by bank loan on mortgage or debentures. The water right can be paid for by the issue of $250,000 in ordinary or deferred shares.

The complete scheme of capitalization will then be as follows:

Existing mortgages	$ 69,440	
Bank loan	83,278	
Preference shares, 8 per cent	166,620	
Ordinary shares to owners	250,000	
		$569,338

The apportionment of revenue will be as follows:

Working expenses: —		
Wages, materials, taxes, and administration	$8,325	
Amortization of plant and renewals: —		
Buildings, 10 per cent on $13,325.....	1,335	
Ironworks, 5 per cent on $65,000.....	3,250	
Machinery, 5 per cent on $69,440.....	3,470	
Earthworks, 2½ per cent on $40,000.....	1,000	
		$17,380
Capital charges: —		
Mortgages:—		
Interest at 5 per cent on $69,440.....	$3,470	
Redemption fund: —		
10 per cent on $27,775.....	2,775	
2½ per cent on $41,660.....	1,040	
		$7,285
Bank loan: —		
Interest, 6 per cent on $83,325.....	$5,000	
Redemption fund, 5 per cent.....	4,165	
		$9,165
The share capital: —		
Preference shares $166,620 @ 8 per cent.....	$13,330	
Ordinary shares $250,000 @ 8 per cent.....	20,000	
		$33,330
		$67,160
Revenue: —		
6,000 kw. at $12.50 per kw.		$75,000
Margin		$7,840

This fall costs only $37 per kw. to develop and equip. It is therefore possible to place a considerable value on the water right.

If now the same revenue is obtained from another waterfall (B) which, owing to less favorable natural conditions, will cost $41.25 per kw. to develop and equip = Kr. 150; or from a third fall (C) costing $55.50 per kw. (= Kr. 200, an average cost in Western Norway), then, omitting the ordinary shares altogether, in the case of (C), and valuing the water right at $125,000 in ordinary shares in the case of (B), the account will stand as follows, viz.:

Total cost of development with margin in same proportion as before, B, $291,665, C, $388,885.

Schemes of capitalization: —

	B.	C.
Existing mortgages as before for the sake of comparison	$ 69,440	$ 69,440
Bank loans	111,100	138,875
Preference shares, 8 per cent.	180,525	249,975
Ordinary shares for water right	125,000	.....
Total capitalization	$486,065	$458,290

Apportionment of revenue as follows:

Working expenses: —

Wages, material, taxes, and administration as before.	$ 8,325	$ 8,325
Amortization of plant	11,580	15,440

Capital charges: —

Mortgages as before	$ 7,440	$ 7,290
Bank loans, 6 per cent and 5 per cent.	12,220	15,275
Preference shares, 8 per cent	14,440	20,000
Ordinary shares 8 per cent	10,000	.....
	$64,005	$66,330

Revenue: —

As before	75,000	75,000
Margin	$10,995	$8,670

(without any dividend for ordinary shares in the case of fall (C)).

The $250,000 ordinary shares in the case of fall A and the $125,000 ordinary shares in the case of B, and nothing (by comparison) in the case of C, therefore represents the fair valuation of the water right, and when it is considered that the return on these deferred shares rank after the preference shares and mortgages, and the revenue will gradually rise to 12 per cent on all shares during the currency of the long contract by reason of the accumulation of the sinking funds for extinction of the loans, it must be allowed that the valuation is not excessive.

As, however, it is by no means certain that there exist a very large number of other powers, which can be developed at even so low a cost as to permit of the sale of the energy at $12.50 per kw. (= $9.30 per E.H.P.) per year, or that such will come into

the market, either in Norway or anywhere else, the value of the waterfall (A) may very likely rise much above the value indicated by these estimates. For if the current price of energy in the next few years finds a level at $15.00 per kw.-year, the capitalized value of the undeveloped fall in question would be more than twice that shown in the table.[1]

It may be added that although the above valuation is self-evidently a just one, yet so little attention has been drawn to these remarkably favorable opportunities of producing power, with low capital expenditure and low working costs, that values such as those indicated by the above figures are not always attached to these properties as yet. How long this opportunity of reaping a large increment, on capital combined with intelligence, will remain open, is a matter for the intelligent capitalist, and the Norwegian government to decide between them.

Moreover, the special case cited does not represent the prices ruling for energy at present in any country except Norway. It still seems probable that $12 to $15 per horse-power-year will be the minimum market price for energy for such purposes in America for some years to come, even from the new plants at Niagara and other distributing centers. This is too great to allow of the developments indicated becoming very extensive, especially when we consider that the account is handicapped by rail freights to such places as Niagara Falls. All such matters, however, are subjects for simple commercial calculations, and, beyond calling attention to this unique opportunity, it is not my object to further elaborate such matters here.

It may now be stated as a general proposition that whilst energy at $15 per horse-power-year will remain hard to dispose of for electro-chemical purposes, and will only find a ready market for slowly expanding such industries as already exist, or for

[1] In Norway at the present time an absolutely unparalleled opportunity is offered for a prosperous era of commercial development such as few countries have ever seen, but the people, though highly intelligent in most matters, have not the power to appreciate it in virtue of their national selfishness. Instead of rising as one man to meet this great opportunity, they are hampering the development in every possible way by shortsighted anti-foreign legislation, aimed at the exclusion of foreign capital, a policy which a more advanced order of intelligence would see hurts far more the nation adopting it than it can ever hurt the foreigner, who has other fields for his energies to choose from if he is foolishly excluded from this one.

lighting and motor propulsion in centers of population, on the other hand, energy, which can be produced and sold for $7.50 per horse-power-year, will soon find a ready and an almost unlimited market, if placed on a deep-water site, or in the center of an agricultural district, in almost any part of the globe. Those fortunate possessors of power capable of being fitted out for Kr. 100 per horse-power, and operated for from $0.50 to $1 (such cases actually exist in Norway to my own knowledge) may reckon on about $6.50 to $7 as yearly income from their property and the capital employed in their outfit, sinking and redemption funds, etc. Given the capital and the means of using the power, they may then make a very handsome profit.

I wish here to emphasize the fact that a great and important change in the world's industrial conditions is impending; that under the new conditions, when there will be many processes available, and ample markets for the products (such as nitrates, iron, heavy chemicals and metals), if prices are low enough to compete with the older, non-electric, methods of production, the essential "raw material" of very many industries will come to be more generally regarded as "energy," and not the salt, the ore, the coal, etc., now usually regarded as raw material in such connections. The existence of any natural source of essentially cheap energy in such accessible situations will, in future, be the signal for the establishment of such industries, quite irrespective of the presence of any other raw material. The electrolytic alkali industry, for instance, which at present clusters in the brine districts, and has caused the spending of considerable sums of money in efforts to get cheaper and cheaper forms of energy in such places, could, by leaving the brine districts, and going straight to the selected water-power of Class 1, on deep-water sites, solve its problems once and for all and at greatly less cost.

Any careful and comprehensive calculation will support these facts. In the same way, sulphide ores from Broken Hill district (in the heart of Australia) can be brought half way round the globe to western Norway and treated there by the water-powers more advantageously than by the free waste products of blast furnaces in that country. It is much to be regretted that such a country as Norway, where unique conditions of the kind indicated exist — conditions which, as I have pointed out, are

capable of enormously encouraging the development of all electro-chemical industries in the near future, — should have adopted a manifestly antiquated and retrograde policy towards foreign enterprise, by imposing conditions on foreigners desirous of working in their country which are both unfair and irksome to fulfil.

No such restrictions exist in America, the land of freedom; and it is to be confidently expected that the most favorably placed of the powers already known, and probably a great number of at present neglected smaller ones, will find an early and profitable employment whenever they can be developed cheaply enough.

It is not necessary to refer to other sources of power in detail. Every good maker's catalogue nowadays contains the fullest information about the many forms of machinery available, and the selection of such apparatus for any particular purpose must always be the task of technical experts, having full knowledge of all the requirements, limitations, and conditions in each individual industry. Whenever it is possible, industries will in future congregate at the water-powers; and the gas engine (with comparatively few exceptions in the cases of operations which must be carried out on the spot) will become as obsolete as a source of electrothermal production as the steam engine is already becoming, or as the voltaic battery became at an earlier date. The latter still survives for such uses as telegraphy, household bell work, medical appliances, gold and silver plating, etc., and I suppose that every year actually still sees an increase in the numbers of batteries sold, by reason of a vast general expansion of industry. So, likewise, the steam engine and gas engine will probably survive for such uses as metal refining and the like, where the energy required is a small item of the total costs, and the expenses and risks of transport would be great.

Steam and gas engines are still employed in England for electrolytic alkali production, by carefully elaborated processes in which the wasted energy is brought as low as possible even at the expense of very elaborate and costly apparatus; but the general trend of the great bulk of these industries, I am convinced, will in the future be to the water.

Cheap energy from water-power, easily developed and regu-

lated, on deep water for transport, and as near as may be possible to commercial centers, is the desideratum of the electrolytic and electrothermal industries of the future; and the process of the future will aim not so much at excessive refinements in the economy of energy, but at designing processes which use little apparatus of a costly nature either for upkeep or installation. Such has been the tendency in many industries already, and such, I think, will be the tendency in many more.

A single example will illustrate this condition as applied to the electrolytic industry more fully, and the example selected is by no means the most favorable which might be chosen to support the case. I have already stated that the electrolytic alkali trade employs steam and gas engines in England. It employs mainly water-power of Class 2 in America, and in Germany and France it employs both means of energy production. It is, in fact, just one of those industries which, handling large quantities of materials and products, and not employing an excessive quantity of energy, seems at first sight to lie half way between the various possibilities offered by different sources of power. In the electrolytic production of 2.4 tons of caustic soda and 5.2 tons of bleaching powder, 3.5 tons of salt and 3.3 tons of lime are employed. By the most favorable process extant in respect of low energy consumption, this amount of product will require 1 h.p.-yr. at the terminals of the cell. Allowing for supplementary energy consumption such as cranes, hoists, pumps, and all the numerous paraphernalia of an alkali works, this represents not less than 1.25 h.p.-yr. or the equivalent in boiler or gas engine consumption; or, with losses, say not less than one and a half electrical horse-power-years. For the total of 7.6 tons of product and 6.7 tons of raw material, therefore, there is a difference between Class 1 water-powers at $7.50 per h.p.-yr. and gas engine power at $30 per h.p.-yr., which will leave a margin of $33 on a total of 14.3 tons, or an average of about $2.50 for each ton of raw material and of product handled. This margin is in itself large enough to make it evident that the saving in energy costs would more than cover the extra cost of freights by working at a Norwegian water site in preference to an English or German coal or gas site. This is still more forcibly realized when it is calculated that with this cheap energy the concentration of liquors and similar

subsidiary processes can nowadays be readily carried on in induction apparatus using electrically produced heat instead of coal. But the real difference in favor of the cheap energy site is greater than at first appears, for in all such undertakings (dependent as they are, more or less, on speculative elements and fluctuating markets), the earlier limits to the practicable extent of operations are usually found in the amount of capital which can be made available for a given prospective enterprise. Large capitals are difficult to obtain for any new enterprise. Beyond a certain point, the capital becomes unwieldy, and the business risk appears too great, except in the case of old established concerns which have grown slowly. Now, dollar for dollar, the capital expended in a water-power (of Class 1) will go about four times as far as the same money spent in either steam or gas engine plant. The outlay for power plant, in installations of the industries we are considering, in most cases, represents from one-half to two-thirds of the entire outlay. When such power plant is located and designed for a special purpose, it is not at all readily adaptable to any other purpose in case of failure of the first. Therefore for a concern with limited capital, struggling to introduce a new industry (often against skeptical or prejudiced opposition), the scheme which can show about twice the output for the same expenditure of capital, and at the same time fully equal the other in ton for ton economy of working costs, has an overwhelming advantage which only requires to be correctly stated to be at once appreciated.

My belief that this subject has not received nearly enough attention and that its great importance to the early expansion of electrolytic and electrothermal industries has been overlooked, must be my excuse, if excuse is needed, for this chapter of special pleading in favor of a single class of energy production.

The following table will be useful for ready comparisons of prices of electric energy in electrical horsepower and kilowatt-years and hours, the various forms usually dealt with by electrochemical engineers. The prices are compared in the money of four countries, including Norwegian kroners.

TABLE 8.—FOR READY COMPARISON OF PRICES OF ELECTRIC ENERGY.

(N.B. Rate of Exchange: $1 = 4 s. — = Mks. 4.04 = Kr. 3.64.)

Per Kilowatt-								Per Electrical Horse Power- (746 Watts).							
Year.				Hour.				Year.				Hour.			
Dollars.	£. s. d.	Marks.	Kroners (Norwegian)	Cents (100 = $)	Pence (240 = £.)	Pfennigs (100 = Mk).	Ore.(100 = Kr.) (Norwegian).	Dollars.	£. s. d.	Marks.	Kroners (Norwegian).	Cents (100 = $)	Pence (240 = £).	Pfennig (100 = Mk.)	Ore.(100 = Kr.) (Norwegian).
1	4	4.04	3.64	.011	.006	.046	.042	.75	3	3.03	2.73	.009	.004	.035	.031
2	8	8.08	7.28	.02	.01	.09	.08	1.50	6	6.06	5.46	.018	.008	.069	.062
3	12	12.12	10.92	.03	.02	.14	.12	2.25	9	9.09	8.19	.03	.01	.10	.09
4	16	16.16	14.56	.05	.02	.18	.17	3.00	12	12.12	10.92	.03	.02	.14	.12
5	1	20.20	18.20	.06	.03	.23	.21	3.75	15	15.15	13.60	.04	.02	.17	.16
6	1.4	24.24	21.84	.07	.03	.28	.25	4.50	18	18.18	16.38	.05	.03	.21	.19
7	1.8	28.28	25.48	.08	.04	.32	.29	5.25	1.1	21.21	19.11	.06	.03	.24	.22
8	1.12	32.32	29.12	.09	.04	.37	.33	6.00	1.4	24.24	21.84	.07	.03	.28	.25
9	1.16	36.36	32.76	.10	.05	.41	.37	6.75	1.7	27.27	24.57	.08	.04	.31	.28
10	2.	40.40	36.40	.12	.06	.46	.42	7.50	1.10	30.30	27.30	.09	.04	.35	.31
11	2.4	44.44	40.04	.13	.06	.51	.46	8.25	1.13	33.33	30.03	.10	.05	.38	.34
12	2.8	48.48	43.68	.14	.07	.55	.50	9.00	1.16	36.36	32.76	.10	.05	.41	.37
13	2.12	52.52	47.32	.15	.07	.60	.54	9.75	1.19	39.39	35.49	.11	.05	.45	.40
14	2.16	56.56	50.96	.16	.08	.65	.58	10.50	2.2	42.42	38.22	.12	.06	.48	.44
15	3.	60.60	54.60	.17	.08	.69	.62	11.25	2.5	45.45	40.95	.13	.06	.52	.47
16	3.4	64.64	58.24	.18	.09	.74	.66	12.00	2.8	48.48	43.68	.14	.07	.55	.50
17	3.8	68.68	61.88	.19	.09	.78	.71	12.75	2.11	51.51	46.41	.15	.07	.59	.53
18	3.12	72.72	65.52	.20	.10	.83	.75	13.50	2.14	54.54	49.14	.16	.07	.62	.56
19	3.16	76.76	69.16	.22	.11	.88	.79	14.25	2.17	57.57	51.87	.16	.08	.66	.59
20	4.	80.80	72.80	.23	.11	.92	.83	15.00	3.	60.60	54.60	.17	.08	.69	.62
21	4.4	84.84	76.44	.24	.12	.97	.87	15.75	3.3	63.63	57.33	.18	.09	.72	.65
22	4.8	88.88	80.08	.25	.12	1.01	.91	16.50	3.6	66.66	60.06	.19	.09	.76	.68
23	4.12	92.92	83.72	.26	.13	1.05	.96	17.25	3.9	69.69	62.79	.20	.09	.79	.72
24	4.16	96.96	87.36	.27	.13	1.10	1.	18.00	3.12	72.72	65.52	.21	.10	.83	.75
25	5.	101.	91.	.29	.14	1.15	1.04	18.75	3.15	75.75	68.25	.22	.11	.86	.78
26	5.4	105.04	94.64	.30	.14	1.20	1.08	19.50	3.18	78.78	70.98	.22	.11	.90	.81
27	5.8	109.08	98.28	.31	.15	1.25	1.12	20.25	4.1	81.81	73.71	.23	.11	.93	.84
28	5.12	113.12	101.92	.32	.15	1.29	1.16	21.00	4.4	84.84	76.44	.24	.12	.97	.87
29	5.16	117.16	105.56	.33	.16	1.34	1.20	21.75	4.7	87.87	79.17	.25	.12	1.	.90
30	6.	121.20	109.20	.34	.17	1.38	1.25	22.50	4.10	90.90	81.90	.26	.12	1.04	.93
31	6.4	125.24	112.84	.35	.17	1.43	1.29	23.25	4.13	93.93	84.63	.27	.13	1.07	.96
32	6.8	129.28	116.48	.36	.18	1.48	1.33	24.00	4.16	96.96	87.36	.28	.13	1.10	1.
33	6.12	133.32	120.12	.38	.18	1.52	1.37	24.75	4.19	99.99	90.09	.28	.14	1.14	1.03
34	6.16	137.36	123.76	.39	.19	1.57	1.41	25.50	5.2	103.02	92.82	.29	.14	1.17	1.06
35	7.	141.40	127.40	.40	.19	1.61	1.45	26.25	5.5	106.05	95.55	.30	.14	1.21	1.09
36	7.4	145.44	131.04	.41	.20	1.66	1.49	27.00	5.8	109.08	98.28	.31	.15	1.24	1.12
37	7.8	149.48	134.68	.42	.20	1.71	1.54	27.75	5.11	112.11	101.01	.32	.15	1.28	1.15
38	7.12	153.52	138.32	.43	.21	1.75	1.58	28.50	5.14	115.14	103.74	.33	.16	1.31	1.18
39	7.16	157.56	141.96	.45	.22	1.80	1.62	29.25	5.17	118.17	106.47	.34	.16	1.35	1.21
40	8.	161.60	145.60	.46	.22	1.84	1.66	30.00	6.	121.20	109.20	.34	.16	1.38	1.24
41	8.4	165.64	149.24	.47	.23	1.89	1.70	30.75	6.3	124.23	111.93	.35	.17	1.42	1.28
42	8.8	169.68	152.88	.48	.23	1.94	1.74	31.50	6.6	127.26	114.66	.36	.17	1.45	1.31
43	8.12	173.72	156.52	.49	.24	1.98	1.78	32.25	6.9	130.29	117.39	.37	.18	1.48	1.34
44	8.16	177.76	160.16	.50	.24	2.03	1.83	33.00	6.12	133.32	120.12	.38	.18	1.52	1.37
45	9.	181.80	163.80	.51	.25	2.07	1.87	33.75	6.15	136.35	122.85	.39	.19	1.55	1.40
46	9.4	185.84	167.44	.52	.25	2.12	1.91	34.50	6.18	139.38	125.58	.40	.19	1.59	1.43
47	9.8	189.88	171.08	.54	.26	2.17	1.95	35.25	7.1	142.41	128.31	.40	.19	1.62	1.46
48	9.12	193.92	174.72	.55	.26	2.21	1.99	36.00	7.4	145.44	131.04	.41	.20	1.66	1.49
49	9.16	197.96	178.36	.56	.27	2.26	2.03	36.75	7.7	148.47	133.77	.42	.20	1.69	1.52
50	10.	202.	182.	.57	.28	2.31	2.08	37.50	7.10	151.50	136.50	.43	.21	1.73	1.56

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